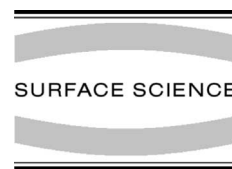




ELSEVIER

Surface Science 482–485 (2001) 90–95



www.elsevier.nl/locate/susc

# Surface enhanced infrared absorption of CO on smooth iron ultrathin films

Andreas Priebe, Gerhard Fahsold, Annemarie Pucci \*

*Kirchhoff-Institut für Physik, Universität Heidelberg, Albert-Ueberle-Strasse 3-5, D-69120 Heidelberg, Germany*

---

## Abstract

We have developed preparation procedures which suppress island growth of Fe on MgO(001) in ultrahigh vacuum. The resulting smooth Fe(001) films of few nanometer thickness have been exposed to CO. The infrared broadband transmission at normal incidence strongly changes with CO exposure. At about  $2050\text{ cm}^{-1}$ , i.e. in the stretching region of CO on on-top sites, enhanced infrared absorption with a Fano-like line shape is observed. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Infrared absorption spectroscopy; Vibrations of adsorbed molecules; Surface electronic phenomena (work function, surface potential, surface states, etc.); Iron; Carbon monoxide; Metallic films

---

Adsorbates on metal-island films can show surface enhanced Raman scattering (SERS) [1] and surface enhanced infrared (IR) absorption (SEIRA) [2–6]. Enhancement is supposed to be due to field enhancement [7] and due to a chemical effect. The chemical contribution partially originates from static charge transfer [8]. The results presented here point to another important contribution to the enhancement of oscillator strength, which is the dynamic interaction of adsorbate vibrations with the electron–hole continuum from the substrate. This kind of interaction corresponds to the Fano effect [9], which leads to an asymmetric line shape. Such shapes of vibrational lines of adsorbates on metal crystals were reported for the first time by Chabal [10]. Langreth [11,12] de-

veloped a theory for the interpretation of the Fano-like line shape of vibrations that interact with the external field. However, even for adsorbate vibrations that do not interact with the external field, like the frustrated translation of CO on copper in grazing-incidence reflection experiments [13], asymmetric absorption lines were measured. The respective theory by Persson [14] assumes friction forces between adsorbates and electrons.

The asymmetric SEIRA lines of CO on smooth Fe(001)/MgO(001) we have measured will be shown here and will be interpreted in the framework of the non-adiabatic theory [11,12], i.e. an interaction of the stretching vibration with the external field is supposed. With this supposition we account for the possibility that the CO molecules are not really perpendicularly adsorbed with respect to the macroscopic surface normal, e.g. due to their mutual repulsion at higher coverages [15].

---

\* Corresponding author. Fax: +49-6221-549262.

E-mail address: a.pucci@urz.uni-heidelberg.de (A. Pucci).

The in situ experiments are performed with the help of a combination of a vacuum Fourier-transform-IR spectrometer (Bruker IFS 66 v/S) with midrange mercury–cadmium–telluride detector and of an ultrahigh vacuum (UHV) chamber (base pressure  $< 2 \times 10^{-8}$  Pa). In detail, the experimental set-up has been described in Ref. [16]. This set-up allows IR transmission spectroscopy during thin film growth under UHV conditions and surface structure analysis by low energy electron diffraction (LEED). The metal film thicknesses are calculated from the deposition time and the rate (typically 0.15 nm/min assuming Fe bulk density), which is calibrated with a quartz microbalance. Substrate temperatures were measured by a chromel–alumel thermocouple attached to the sample holder. The MgO(001) substrates are prepared in air by cleavage of  $7 \times 7 \times 15$  mm<sup>3</sup> sized single crystals. After cleavage the substrates were transferred to high vacuum within few minutes and were baked for 20 h at  $\sim 473$  K. After transfer to UHV they were degassed at  $\sim 723$  K for 2 h. The surfaces of these MgO substrates appear crystalline as judged from LEED (see Fig. 1a). The smooth Fe films were prepared on them by subsequent depositions at two different temperatures [17]. For example, 3 nm thick film an initial layer of 1.5 nm thickness was grown while the substrate was held at room temperature. Then, the temperature was raised to 670 K and Fe was deposited up to the final thickness. In Fig. 1b the typical LEED patterns of a film prepared in this special way are shown. From these patterns, from a detailed IR transmission analysis, and from ex situ atomic force microscopy we deduce that the initially rough film is smoothed by the second deposition step at higher temperature [17]. This temperature should not be too high to avoid break up of the film. After Fe film preparation the samples were cooled to about 100 K and exposed to CO (purity 99.997 vol%,  $p_{\text{CO}} \approx 2 \times 10^{-6}$  Pa). During exposure we measured the transmittance change of the sample with a resolution of  $4 \text{ cm}^{-1}$  (50 scans per spectrum sampled in 14 s). The IR transmittance spectra shown here (see Fig. 2) have been measured at normal incidence. The transmittance change saturates at CO exposures of about 4.5 L (1 L(Langmuir) =  $1.333 \times 10^{-4}$  Pa s) for the

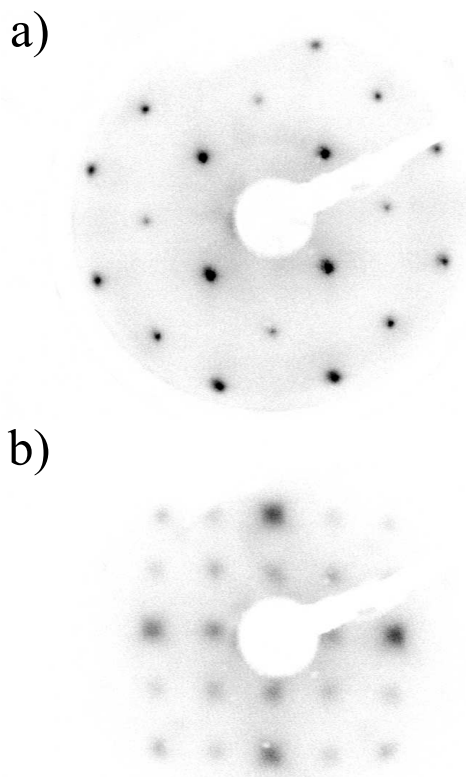


Fig. 1. LEED patterns at primary energy of 174 eV for (a) the MgO substrate and (b) for the 3 nm Fe on this substrate.

smooth iron films on MgO. From MgO cleavage to CO exposure the experiments were repeated for the individual iron thicknesses.

At room temperature the IR transmittance (relative to the substrate transmittance) of the 3 nm smooth Fe film of Fig. 1b is about 0.5 for wave numbers above  $2000 \text{ cm}^{-1}$  which is similar to the corresponding transmittance ( $\approx 0.55$ ) of 3 nm Fe grown on UHV-cleaved MgO at room temperature. The IR-spectral slope indicates continuity of the metal film as discussed in Ref. [17,18]. The room-temperature spectrum can be numerically reproduced with a Drude-like dielectric function based on bulk data [19] with small modifications to account for the size effects [18,20]. However, surface relaxation is negligibly small for the smooth 3 nm thick film. Our calculation of relaxation rates

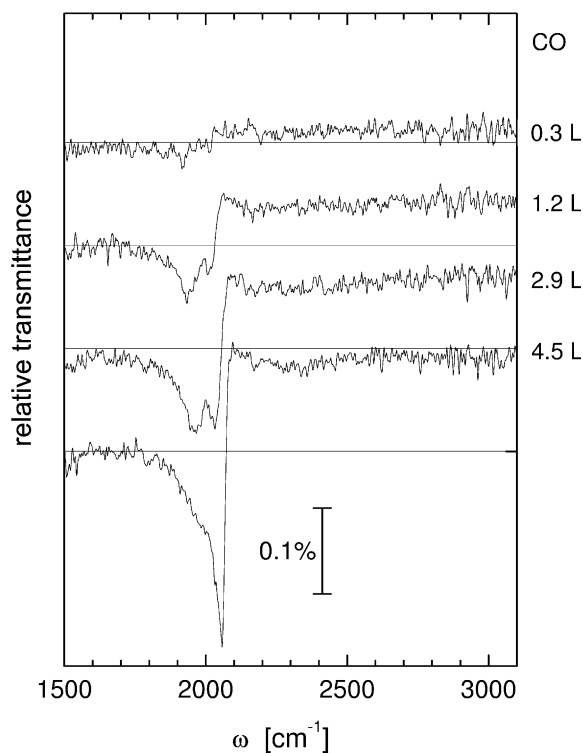


Fig. 2. Normal incidence relative IR transmittance versus frequency  $\omega$  (given in wave number units) of CO adsorbed at 100 K on 3 nm Fe(001) on MgO(001) for various exposures as indicated. The spectra are shown as they were measured. The horizontal lines mark a transmittance of 100% for the individual spectra.

from IR spectra is explained in more detail elsewhere [18].

Exposure of CO at about 100 K leads to significant base line changes and to the occurrence of CO-stretch lines. Fig. 2 shows transmittance spectra of CO/Fe/MgO(001) for CO exposures from 0.3 L to about 4.5 L. The most surprising feature is the considerable intensity of the absorption lines. The observed oscillator strength contradicts the usual representation of CO adsorbed perpendicularly to the surface, which is assigned to vibrational frequencies above 2000  $\text{cm}^{-1}$  [21]. The frequency of the stronger transmission minimum well matches the electron-energy-loss (EEL) data for CO on Fe(001) with the frequency 2055  $\text{cm}^{-1}$  for CO on the on-top site at saturation exposure [21]. The interpretation of the

broader feature  $\leq 2000 \text{ cm}^{-1}$  is unclear. With EEL spectroscopy it could not be resolved. However, the development of both peak positions with CO exposure does not agree with the findings for CO adsorption on the single crystal surfaces Fe(110) and Fe(111) [22,23]. Possibly, the broad peak  $\leq 2000 \text{ cm}^{-1}$  belongs to CO on bridge sites, which could be promoted by strain in the epitaxial Fe(001) film. It is known that epitaxial iron films on MgO(001) below 30 nm thickness have lattice constants different to the bulk value [24]. CO vibrational frequencies sensitively change with the atomic structure parameters as it is shown for CO on ultrathin Fe films on Cu(100) [25]. For Fe films thicker than 6 nm we detect only the on-top peak in the frequency region under investigation [26,27]. Concerning the total strength of the CO stretching signal, it is important to note that we repeated the experiments for 3 nm (and also for other thicknesses) and we always got the same spectra within experimental errors [26]. Since each cleavage of MgO should produce another step density on the substrate surface we do not believe that the strong CO signal is due to such steps. In addition, for Fe films with tears that arise from an unfavourable preparation step at too high temperatures the signal strength is similar to that for the smooth films [26]. Therefore we suppose that the main part of the CO signal is due to CO on the film surface which consists of (001) terraces [17]. This assumption contradicts any influence of field enhancement. Since a reasonable amount of static charge transfer also cannot explain the observed signal strength it should be caused by non-adiabatic interaction which also fits the observed asymmetric line shape and the baseline change.

Accordingly, we will compare the experimental relative transmittance at normal incidence after CO exposure to spectra calculated with Fano-like susceptibility

$$\chi(\omega) = \chi_{\text{OSC}}(\omega) + \chi_{\text{BKG}}(\omega) \quad (1)$$

that corresponds to the generalized susceptibility function (with the resonant background) introduced by Langreth [11] for one adsorbed molecule. One kind of oscillator contributes with

$$\chi_{\text{OSC}}(\omega) = \omega_{\text{IP}}^2 \frac{(1 + i\omega\tau)^2}{(\omega_0^2 - \omega^2 - i\omega\gamma)} \quad (2)$$

where

$$\omega_{\text{IP}} = Z \sqrt{\frac{n_a}{d_a m_{\text{red}}}} \quad (3)$$

is the ionic plasma frequency with the dynamic effective charge  $Z$  that could be changed by non-adiabatic intensity borrowing. The circular frequency is denoted by  $\omega$ ,  $\omega\tau$  is the phase delay of the electronic contribution to the dynamic charge due to the non-adiabatic interaction,  $\gamma$  is the line width of the Lorentzian at  $\tau = 0$ , and  $\omega_0$  is the resonance frequency. The other parameters of the ionic plasma frequency are the surface density  $n_a$  of adsorbates, the thickness  $d_a$  of the adsorbate layer, and the reduced mass  $m_{\text{red}}$  of the vibrational mode (here: C–O stretching). The background susceptibility is

$$\chi_{\text{BKG}}(\omega) = \omega_{\text{IP}}^2 \frac{\tau}{\gamma} \left( \frac{\Delta Z}{Z} + i\omega\tau \right) \quad (4)$$

with the electronic contribution  $\Delta Z$  to the total dynamic effective charge  $Z$ .  $\text{Im}(\chi_{\text{OSC}} + \chi_{\text{BKG}})$  has a Fano line shape.

The two oscillators of the experimental spectra are described with two contributions of type (1) and were added to a non-resonant background of about 1. These susceptibilities are used as inputs for the CO layer (with  $d_a = 0.24$  nm, i.e. twice the C–O distance) in the layer stack CO/Fe/MgO the transmittance spectra of which is calculated with the software package *SCOUT* [27]. The iron film dielectric function is supposed as Drude-like with a total relaxation rate

$$\omega_\tau = \omega_{\tau 0} + \delta\omega^2, \quad (5)$$

with  $\omega_{\tau 0}$  corresponding to  $25 \text{ cm}^{-1}$  at  $100 \text{ K}$ <sup>1</sup> before exposure and  $\omega_\tau + \Delta\omega_\tau$  after exposure, respectively. Eq. (5) considers the frequency dependence of the relaxation rate at higher energies [18]. The room temperature bulk data [19] give  $\delta$  cor-

responding to  $3.2 \times 10^{-4} \text{ cm}$ , however, at  $100 \text{ K}$  it should be lower. According to our findings for Fe grown on UHV-cleaved MgO [18] the plasma frequency  $\omega_{\text{FP}}$  for continuous iron films is used to be equal to  $\beta\omega_p$  with  $\beta = 1.26$  as the limit for high thickness. The plasma frequency  $\omega_p(\omega)$  is derived from the iron bulk data [18,20]. Any charge transfer due to adsorption would lead to a change  $\Delta\beta\omega_p$  of the film plasma frequency  $\omega_{\text{FP}}$ .

The MgO thickness was 3 nm for the experiment of the Figs. 2 and 3. The input dielectric function for the MgO consists of a relative

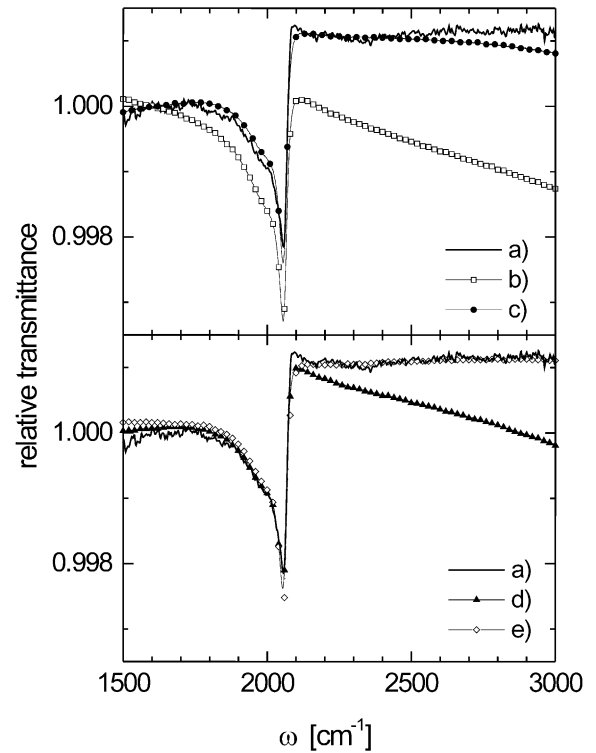


Fig. 3. Normal incidence relative IR transmittance spectra of CO on 3 nm Fe(001) on MgO(001) at  $100 \text{ K}$  at saturation exposure of  $4.5 \text{ L}$  compared to calculations: (a) experimental curve for saturation exposure (200 scans), (b–e) calculations with various slight changes of iron film properties, (b) iron film parameters unchanged by the adsorbate and  $\delta = 2 \times 10^{-4} \text{ cm}$ , (c)  $\Delta\omega_\tau$  corresponds to  $14 \text{ cm}^{-1}$ ,  $\Delta\beta = -0.0025$ , and  $\delta = 2 \times 10^{-4} \text{ cm}$ , (d)  $\Delta\omega_\tau$  corresponds to  $14 \text{ cm}^{-1}$ ,  $\Delta\beta = -0.001$ , and  $\delta = 3.2 \times 10^{-4} \text{ cm}$ , (e)  $\Delta\omega_\tau$  corresponds to  $12 \text{ cm}^{-1}$ ,  $\Delta\beta = -0.0038$ , and  $\delta = 1 \times 10^{-4} \text{ cm}$ . For other parameters see text.

<sup>1</sup>  $\omega_{\tau 0}$  at  $100 \text{ K}$  was estimated from the dc resistivities of iron at  $273 \text{ K}$  and at  $77 \text{ K}$  [28], and from  $\omega_{\tau 0}$  at  $300 \text{ K}$  [16].

dielectric constant of 2.84 for the background, the one-phonon absorption at  $405\text{ cm}^{-1}$ , and multi-phonon contributions described by three weak Brendel oscillators [26]. It successfully fits the MgO transmittance and gives reasonable results for the reflectance.

In Fig. 3 the experimental relative transmittance for saturation exposure is compared to calculated relative spectra for various slight changes of the iron film conductivity. The CO parameters used in each case for the first and for the second oscillator are  $\omega_0$  corresponding to 2062 and  $2005\text{ cm}^{-1}$ ,  $\gamma$  corresponding to 33 and  $150\text{ cm}^{-1}$ ,  $\omega_0\tau$  (the so-called asymmetry parameter) equal to 0.64 and 0.6, respectively. The observed size of the signal demands a large ionic plasma frequency. We started with a  $\omega_{\text{IP}}$  value that follows from  $Z = 0.42e$  ( $e$  is the elementary charge) and from  $n_a$  for each oscillator corresponding to one CO per surface Fe atom. By the way, the value  $0.42e$  well fits CO-stretch peak areas of CO on NaCl. Multiplication of  $\omega_{\text{IP}}^2$  by a factor of 14 and of 18 for the first and for the second oscillator, respectively, gives the correct signal strength (see Fig. 3). The enhancement of  $\omega_{\text{IP}}^2$  means that the total dynamic effective charge is increased and that  $\Delta Z$  is at least  $1e$  ( $\approx(\sqrt{14} - 1) \times 0.42e$ ). We have to add that the saturation coverage of CO on Fe(001) at about 100 K is not well known. Our calculations with two oscillators correspond to two CO per surface Fe.

However, we also have to think over that our CO-oscillator input  $\omega_{\text{IP}}$  does not take into account the direction of the vibrational dipole with respect to the external field. The full  $\omega_{\text{IP}}$  value means dipoles parallel to the surface, which is not reasonable for  $\omega_0$  above  $2000\text{ cm}^{-1}$ . Therefore, the real enhancement is much higher than 14 or 18, respectively, and the electronic contribution  $\Delta Z$  is comparable to the total dynamic charge  $Z$  (as supposed in our calculation of the background). Despite the large number of parameters, their different influence on the whole spectrum fixes the results within reasonable intervals. For example the asymmetry parameter of about 0.6 ( $\pm 10\%$ ) gives both the right line shape and a reasonable baseline (see Fig. 3, case b) and it is similar to other findings [3–6,10]. Neglecting the broad os-

cillator at  $2005\text{ cm}^{-1}$  leads to the same asymmetry of the sharp oscillator that we assign to the stretch vibration of CO on on-top sites on Fe(001).

Very slight changes of the two Fe-film conductivity parameters  $\omega_\tau$  and  $\beta$  due to CO exposure allow to reproduce the experimental background better (see Fig. 3, case c). The change of the scattering rate  $\Delta\omega_\tau = 14\text{ cm}^{-1}$  corresponds to a decrease of 0.8% of the specularly parameter in the classical size effect [18] and  $\Delta\beta = -0.0025$  means a charge transfer of  $3.5 \times 10^{-5}$  electrons per surface atom. Because of the experimental errors of our experiment, any further interpretation of these small values of  $\Delta\omega_\tau$  and  $\Delta\beta$  makes no sense, especially, since the correct frequency dependence of the relaxation rate of iron is not known for 100 K. Our calculations with different  $\delta$ -values (see Fig. 3, cases c–e) show that  $1 \times 10^{-4} < \delta < 2.5 \times 10^{-4}\text{ cm}$  (for  $\omega$  in wave numbers) gives a good baseline match. The interval also seems to be reasonable with respect to the higher room temperature  $\delta$ -value.

For an evaluation of our model calculations we would like to mention, that with an analogous calculation method (and  $Z = 0.42e$ ) we have reproduced non-enhanced stretch features in IR reflection at grazing incidence for CO on thick (e.g. 16 nm) Fe on MgO [26].

We have shown for the first time that SEIRA also works on smooth metal films. The underlying mechanism for the enhancement should be the non-adiabatic interaction of adsorbate vibrations with electronic excitations. As an example we have compared the experimental transmittance of CO on a 3 nm film to calculations that are based on a Fano-like susceptibility. With reasonable parameters the experimental data can be reproduced if a large dynamic charge transfer of much more than  $1e$  and an asymmetry parameter of about 0.6 are supposed. More exact values need improved information about the adsorbate geometry on iron.

## Acknowledgements

The authors gratefully acknowledge support by the Deutsche Forschungsgemeinschaft.

## References

- [1] A. Otto, I. Mrozek, H. Grabhorn, W. Akemann, *J. Phys.: Condens. Matter* 4 (1992) 1143.
- [2] M. Osawa, *Bull. Chem. Soc. Jpn.* 70 (1997) 2861.
- [3] O. Krauth, G. Fahsold, A. Pucci, *J. Chem. Phys.* 110 (1999) 3113.
- [4] O. Krauth, G. Fahsold, N. Magg, A. Pucci, *J. Chem. Phys.* 113 (2000) 6330.
- [5] O. Krauth, G. Fahsold, A. Pucci-Lehmann, *J. Molecular Struct.* 482–483 (1999) 237.
- [6] O. Krauth, G. Fahsold, A. Lehmann, *Surf. Sci.* 433–435 (1999) 79.
- [7] V.M. Shalaev, R. Botet, J. Mercer, E.B. Stechel, *Phys. Rev. B.* 54 (1996) 8235.
- [8] P. Kambhampati, A. Champion, *Surf. Sci.* 427–428 (1999) 115.
- [9] U. Fano, *Phys. Rev.* 124 (1961) 1866.
- [10] Y.J. Chabal, *Phys. Rev. Lett.* 55 (1985) 845.
- [11] D.C. Langreth, *Phys. Rev. Lett.* 54 (1985) 126.
- [12] Z.Y. Zhang, D.C. Langreth, *Phys. Rev. B* 39 (1989) 10028.
- [13] C.J. Hirschmugl, G.P. Williams, F.M. Hoffmann, Y.J. Chabal, *Phys. Rev. Lett.* 65 (1990) 480.
- [14] B.N.J. Persson, A.I. Volokitin, *Surf. Sci.* 310 (1994) 314.
- [15] T. Maruyama, Y. Sakisaka, H. Kato, Y. Aiura, H. Yanashima, *Surf. Sci.* 304 (1994) 281.
- [16] O. Krauth, Thesis, Ruprecht-Karls-Universität Heidelberg, 1999.
- [17] G. Fahsold, A. Priebe, A. Pucci, *Appl. Phys. A*, in press.
- [18] G. Fahsold, A. Bartel, O. Krauth, N. Magg, A. Pucci, *Phys. Rev. B* 61 (2000) 14108.
- [19] M.A. Ordal, R.J. Bell, R.W. Alexander Jr., L.L. Long, M.R. Querry, *Appl. Opt.* 24 (1985) 4493.
- [20] G. Fahsold, A. Bartel, O. Krauth, A. Lehmann, *Surf. Sci.* 433–435 (1999) 162.
- [21] C. Benndorf, B. Krüger, F. Thieme, *Surf. Sci.* 163 (1985) L675.
- [22] U. Seip, M.C. Tsai, K. Christmann, J. Küppers, G. Ertl, *Surf. Sci.* 139 (1984) 29.
- [23] W. Erley, *J. Vac. Sci. Technol.* 29 (1981) 472.
- [24] B.M. Lairson, A.P. Payne, S. Brennan, N.M. Rensing, B.J. Daniels, B.M. Clemens, *J. Appl. Phys.* 78 (1995) 4449.
- [25] T. Tanabe, Y. Suzuki, T. Wadayama, A. Hatta, *Surf. Sci.* 427–428 (1999) 414.
- [26] A. Priebe, Diploma Thesis, Ruprecht-Karls-Universität Heidelberg, 1999.
- [27] SCOUT-98, Software Package for Optical Spectroscopy, Soft Science, Aachen, Germany.
- [28] N.W. Ashcroft, N.D. Mermin, *Solid State Phys.*, Saunders College Publishing, 1976.