PHYSICAL REVIEW B VOLUME 55, NUMBER 15 15 APRIL 1997-I

Na intercalation of VSe_2 studied by photoemission and scanning tunneling microscopy

H. E. Brauer, Inger Ekvall, H. Olin, H. I. Starnberg, and Erik Wahlström
Department of Physics, Göteborg University and Chalmers University of Technology, SE-412 96 Göteborg, Sweden

H. P. Hughes
Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, United Kingdom

V. N. Strocov
International Institute of Interphase Interactions, Post Office Box 1146, 194291 St. Petersburg, Russia

(Received 4 December 1996)

In situ Na intercalation of the layered compound VSe_2 has been studied with photoemission and scanning tunneling microscopy. Core-level spectroscopy proves that Na deposited in UHV onto the VSe_2 surface rapidly intercalates, leaving only small amounts at the surface. The scanning tunneling microscopy measurements show that the intercalated Na is not uniformly distributed between the VSe_2 layers, but preferentially in two-dimensional islands. Thus the surface region is divided into intercalated and nonintercalated areas. Holelike features in the intercalated areas are interpreted as locally missing Na. [S0163-1829(97)01415-X]

The layered transition-metal dichalcogenides (TMDC's) are highly anisotropic solids, which exhibit several interesting phenomena. VSe_2 belongs to the group V TMDC's, which are considered as metals due to one single electron per unit cell in the lowest conduction band. VSe_2 crystallizes in the $1T$ structure, with the vanadium in octahedral coordination by the selenium, where the layers are stacked without lateral displacement. Several of the TMDC's of group V are sensitive to periodic lattice distortions of the charge density wave (CDW) type. The formation of CDW's is strongest among the $1T$ structures, and $1T$-TaS_2 and $1T$-$TaSe_2$ both exhibit several commensurate and incommensurate CDW's. VSe_2 also undergoes a transition into a commensurate 4×4 CDW phase below 112 K,[1] but it is relatively weak and VSe_2 behaves clearly different from the tantalum compounds. This difference is due to the narrow V $3d$ band; an occupied band width of only 0.3 eV is reported.[2,3] The corresponding Ta $5d$ bands are much broader, 1.1 and 1.0 eV for $1T$-TaS_2 and $1T$-$TaSe_2$, respectively.[4,5]

One interesting property of the TMDC's is the formation of intercalation complexes, with foreign atoms or molecules between the layers. Charge transfer accomplishes the process, and as the TMDC's form intercalation complexes only with donors, electrons are transferred to the host lattice. The lowest available levels are transition-metal d states, and the altered filling of these bands can have a large influence on the electronic properties. Intercalation with alkali metals is particularly interesting due to their strong tendency to donate their single valence electron, and the possibility to form *in situ* intercalation compounds. This is done by deposition of the alkali in UHV onto the TMDC surface from where it spontaneously intercalates.[6,7]

Layered materials are ideally suited for scanning tunneling microscopy (STM) studies. Local aspects are particularly well investigated, so the formation of CDW's, which is directly connected with a modification of the local density of states near the Fermi level, is well suited for STM studies. CDW's among the TMDC's have been reviewed,[8,9] but STM studies of *in situ* intercalated TMDC's are scarce. Silver intercalation of TaS_2 and NbS_2 is reported,[10,11] where the octahedral coordination of Ta atoms in $1T$-TaS_2 changes into the trigonal prismatic one (characteristic for $2H$ polytypes). The transition temperatures among the various $1T$-TaS_2 CDW phases were also lowered. To our knowledge, the present report is the first STM study of *in situ* alkali-metal intercalation of TMDC's. Such studies, we believe, open promising opportunities to follow the local aspects in the formation and modifications of CDW's.

The core-level spectroscopy measurements were made at the national synchrotron radiation facility MAX-lab, Lund, Sweden. The beamline used incorporates a toroidal grating monochromator with three interchangeable gratings, which provide photons in the energy range 15–200 eV and a modified VSW spherical electron energy analyzer. The incidence angle was 45° and the synchrotron radiation was polarized in the plane of incidence. The electron energy analyzer had ±2° angular acceptance and typically 0.1-eV resolution. The measurements were made at room temperature. In the photoemission experiments, Na was deposited by resistively heating of carefully outgassed commercial SAES getter sources. The exact amount of deposited Na is not known but we estimate that far more Na was deposited than required to obtain monolayer coverage. The clean VSe_2 surface is known to be chemically very inert due to the absence of dangling bonds, but the Na dosed surface was remarkably inert as well. Core-level spectra indicated only slight contamination of the surface and no signs of a significant surface degrading was observed even when over 30 h had passed since the initial deposition. This inertness is probably related to the fact that no alkali overlayer is formed at room temperature, and has been observed for similar alkali-TMDC systems.[12–15] The hexagonal low-energy electron diffraction (LEED) pattern remained sharp but fainter after intercalation and no superlattice spots were seen.

STM measurements were made in a commercial variable temperature ultrahigh vacuum STM from Omicron Vakuum-

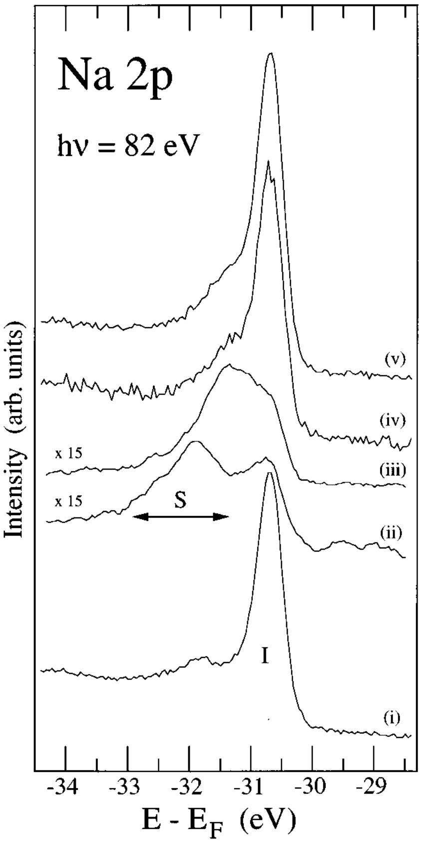

FIG. 1. Na $2p$ core-level spectra recorded with $h\nu=82$ eV. Intercalation and surface related spectral features are labeled I and S, respectively. The spectra were recorded at normal emission except (ii) and (iii) where the emission angle was 75°. The timing relative to the initial Na deposition of the measurements is given in parentheses below. (i) Na $2p$ spectrum immediately after the initial Na deposition ($t=0$). (ii) Na $2p$ spectrum with $\theta=75°$ ($t=0.5$ h). (iii) Na $2p$ spectrum with $\theta=75°$ ($t=13$ h). (iv) Na $2p$ spectrum ($t=16$ h). (v) Na $2p$ spectrum after a second Na deposition made 17 h after the initial ($t=17$ h).

physik GmbH. Na was evaporated from a calibrated Na source (specially designed for this system) of the brakeseal glass ampoule type (ABCR) by resistively heating. The evaporation was controlled by a shutter. The source evaporates 1 ML in about 11 min, as calibrated from work-function measurements and LEED patterns of a Cu(111) surface following Tang *et al.*[16] The base pressure in the UHV chamber was 1×10^{-10} mbar and the pressure never rised during evaporation. The sample was cleaved in air and immediately placed in the fast entry load lock chamber. It was heated to ~350 °C to remove contaminations. STM tips were electrochemically etched W tips, cleaned by heating inside the UHV chamber.[17] All experiments were made at room temperature. The sign of V_{bias} corresponds to sample voltage. All images are slope corrected. Atomic resolution images are distortion corrected within the STM measurement program.

Na $2p$ core-level spectra were recorded with $h\nu=82$ eV to monitor the deposition and to follow the intercalation process (Fig. 1). After the initial Na depositions (2×2 min at 6.0 A), two spectral features are seen, spectrum (i). In analogy with other Na-TMDC studies the intense peak "I" is attributed to intercalated Na, while the weaker structure appearing with higher binding energy (BE) originates from Na at the surface.[18–20] The surface component is shifted 1.1 eV relative to the intercalation peak. The designation of the two peaks is confirmed in spectrum (ii), where the emission angle is 75°, which suppresses the I peak relative to the surface peak. Also, at least two surface components are present, shifted 1.2 and 1.8 eV relative to the I peak. A possible third component shifted 0.8 eV is too weak to be indubitably confirmed. The dominance of peak I in spectrum (i) clearly demonstrates that only a minute fraction of the deposited Na remains at the surface, as electrons emitted from intercalated Na must penetrate at least one VSe_2 layer (about 5 Å thick). The emission angle is 75° also in spectrum (iii). The intensities of the spectral features have not changed much compared to spectrum (ii), but the main surface component shows a significant shift towards lower BE by 0.5 eV. The two surface components from spectrum (ii) remain, but only as weak shoulders. In addition to the main surface component (shifted 0.7 eV relative to I) there might be a further species present shifted 0.3 eV further towards lower BE, but too weak to be indubitably confirmed. The behavior of the surface peaks shows that the state of Na at the surface changes with time, possibly by reaction with residual gases. In spectrum (iv), the I peak is very similar to that in spectrum (i). The emission from surface Na agrees well with spectrum (iii), though no clear structure is observed. Thus, it is clear that the tail on the I peak cannot entirely be due to the intrinsic asymmetry arising from the screening of the core hole by electrons in the conduction band.[21,22] After a second Na deposition, spectrum (v), the I peak was more intense but the surface emission appears unaffected. 10 h later, the I peak was weaker (not shown), but no significant change in the overall line shape was observed.

It is evident that Na easily intercalates when deposited onto the VSe_2 surface at room temperature. The peak originating from intercalated Na did not change much with time or after additional depositions, the intensity was modulated but not drastically. The Na at the surface exhibits a time dependence and goes through transitions to species with lower BE. Additional depositions did not alter the surface composition and the lower BE configuration appears to be stable. The stoichiometry or concentration of intercalated Na was estimated by calculating the relative core-level intensities of the Na $2p$ compared to Se $3d$, normalized by photoemission cross sections.[23] After the first deposition the stoichiometry was $Na_{0.25}VSe_2$. From spectra recorded 6 and 16 h later a stoichiometry $Na_{0.20}VSe_2$ was deduced, which show that parts of the intercalated Na had diffused more deeply into the bulk. The second deposition resulted in $Na_{0.30}VSe_2$, but 10 h later the stoichiometry was $Na_{0.20}VSe_2$ again due to diffusion into the bulk. The amount of Na at the surface is small but cannot be accurately estimated due to the weak intensity. Photoelectrons from the Se $3d$ and intercalated Na $2p$ levels have different escape depths as the outermost layer consists of Se atoms and the Na atoms reside in the van der Waals gaps. Thus the signal from the Na $2p$ level is most likely attenuated and the calculated stoichiometries ought to be lower limits. Diffraction effects could also influence the

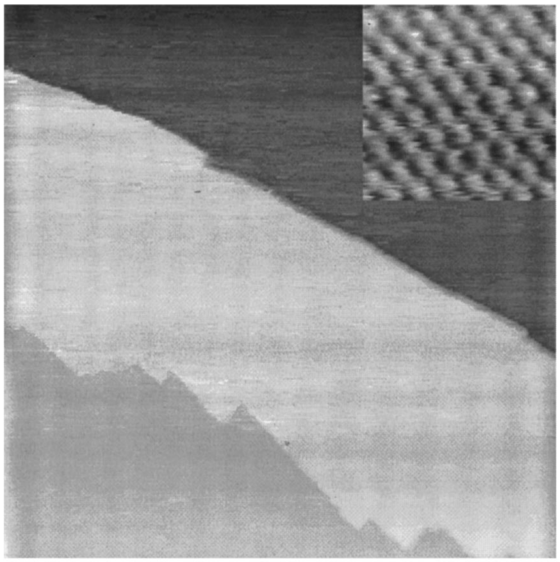

FIG. 2. STM image of VSe_2 showing large flat areas separated by steps. The step at the bottom of the image is a single step, while the step at the top is multiple. $V_{\mathrm{bias}}=-0.13$ V, $I=0.84$ nA, scan range 800×800 nm^2. Inset: Atomic resolution scan of VSe_2. $V_{\mathrm{bias}}=-0.11$ V, $I=1.71$ nA, scan range $\sim2.8\times2.8$ nm^2.

peak intensities, so the calculated stoichiometries should be considered as approximate, but the observed trend should be reliable.

STM images of the clean VSe_2 surface show large ($\sim$600 nm) flat and rather defect free areas (Fig. 2). The images are in good agreement with previous studies,[8,9] though the temperature is well above the onset of the 4×4 CDW. Steps in the surface are single layer as well as multilayer steps. STM images immediately after evaporation of Na for 10 min ($\leqslant$1 ML) show two distinctly different features. The first, dark areas of reduced topographic height with a lateral extension of 15 nm up to $>$100 nm, could be seen in all pictures (Fig. 3). Atomic resolution images on the two types of areas (dark and bright) show no differences. The step height is estimated to $\sim$1.6 Å, much smaller than expected if originating from a VSe_2 layer step (over 6 Å). The second appeared as small ($\sim$1–2 nm) holelike features, spread out on the surface in the bright areas. These holes are not due to intercalation-induced lattice defects, since images show atomic resolution inside these holes with no distortion of the lattice as seen in Fig. 4. The holes are less deep than the large dark areas, $\sim$1.0 Å. No sign of Na at the surface is observed in the STM images. The images do not change with time, but look very much the

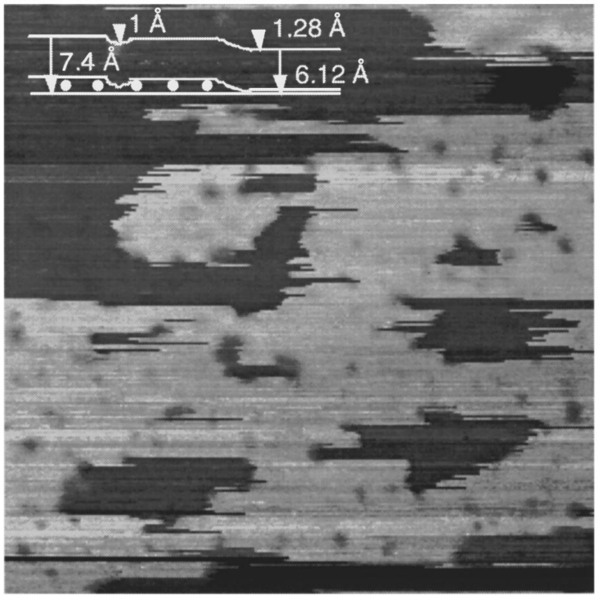

FIG. 3. STM image of Na intercalated VSe_2. Large dark areas and small holes are distributed randomly across the surface. $V_{\mathrm{bias}}=-0.06$ V, $I=2.32$ nA, scan range 100×100 nm^2.

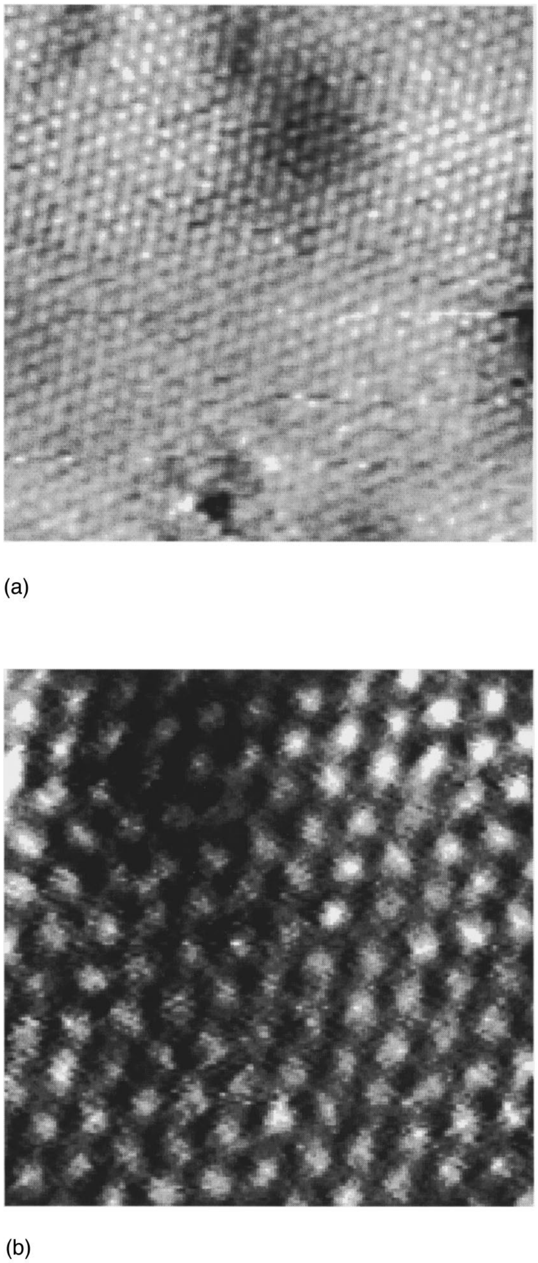

FIG. 4. STM images of Na intercalated VSe_2 showing the atomic lattice. Inside the holes the atomic lattice is undistorted, showing that the holes are not due to a lattice defect. (a) Scan range $\sim9\times9$ nm^2, $V_{\mathrm{bias}}=-0.06$ V, $I=2.32$ nA. Inside the hole, atoms are clearly resolved. Note the lattice defect in the bottom of the image. (b) Scan range $\sim4.2\times4.2$ nm^2, $V_{\mathrm{bias}}=-0.06$ V, $I=2.32$ nA.

same one week after the Na deposition; apart from that the sample gradually becomes contaminated. A second deposition (equivalent to another layer of Na) was made one week after the initial one, but the results were not significantly different from the first images.

Earlier neutron diffraction measurements indicate that the a axis lattice parameter should be expanded upon intercalation. Two structural phases of Na intercalated VSe_2 are reported, with Na in either trigonal prismatic or octahedral coordination between the layers.[24] The octahedral structure, $3R$(II), is obtained for high concentration of intercalated Na ($a=3.73$ Å), with the trigonal prismatic structure, $3R$(I), obtained for lower concentrations ($a=3.48$ Å). Based on the photoemission estimates, it is more likely that the trigonal prismatic structure is achieved. This lattice expansion (from 3.35 to 3.48 Å) cannot be confirmed from the images due to the electronic drift in the microscope that causes lateral distortions of the images, making absolute distance measurements difficult. As Na enters between the VSe_2 layers, the interlayer distance increases with 1.28 Å for the $3R$(I) structure.[24] The bright and dark areas and the holes would then correspond to intercalated and nonintercalated areas. The topographic height is increased in the regions where intercalated Na is present in the first van der Waals gap as compared to when Na is absent; see inset of Fig. 3. This leads to steps smaller than the single layer thickness. The step height is somewhat larger than the expected 1.28 Å, but this could possibly be induced by different charge density in the two regions. The lateral extension of a step is of the order of a few nm, i.e., the size of the holes. The holes will then be less deep than the steps since the lateral extension is too small to restore the VSe_2 layer separation to the nonintercalated value. This means that the top VSe_2 layer is ''buckled'' due to nonuniform distribution of intercalated Na. However, the possibility that the holes are due to excess V present between the layers must also be considered. Then the V atom would induce a local perturbed region, which the Na atoms avoid. No detectable lattice distortion due to the absence of Na is expected in the shallow holes; anyway, this distortion would be beyond the limit of the STM technique. A second evaporation need not give large differences, as the Na could be more closely packed in the areas where Na is intercalated, or Na could diffuse into the bulk. Then the relation between dark and bright areas could be fairly constant, but for repeated depositions a more uniform distribution is eventually expected. If the Na atoms are densely packed in the intercalated areas, the estimation of $Na_{0.2}VSe_2$ from the photoemission data does not contradict the STM images, where ~50% of the surface area seems to be intercalated. The photoemission estimate averages the Na $2p$ signal from intercalated and nonintercalated areas. The Na $2p$ signal is compared to the Se $3d$ signal, but Se atoms are present in both areas. Thus, a direct comparison between STM and photoemission results is not relevant, but a more complementary picture is provided.

The apparent absence of Na on the surface in the STM images might be due to the fact that less Na was probably evaporated in the STM than in the photoemission measurement. As the STM is highly sensitive, this indicates that very little Na was present on the surface, but if trapped at steps or other defects it would be difficult to image the Na atoms.

It is interesting that the only available study that probes the surface geometric structure (Na intercalation of $1T$-TaS_2 and $2H$-TaS_2 by surface extended x-ray absorption fine structure),[19] reports that the intercalated Na is positioned in octahedral coordination and that trigonal prismatic sites could be excluded. This somewhat contradicts our interpretation of the STM images, but it is not certain that the findings from Na intercalation of $1T$-TaS_2 and $2H$-TaS_2 could be strictly applicable to $1T$-VSe_2. The a-axis lattice parameter should then also be further expanded, which would be easier to observe. More important though is that the interlayer expansion would be 0.76 Å,[24] i.e., only half the height of the steps in the images. Under the circumstances, our interpretation seems plausible, but more studies are needed until this matter is straightened out.

In conclusion, we report STM measurements of *in situ* Na intercalation of the layered compound VSe_2. Intercalation is verified by core-level spectroscopy. The STM images show that the intercalated Na is not uniformly distributed between the VSe_2 layers. Instead, the Na forms islands or ''two-dimensional clusters'' dividing the surface region into intercalated and nonintercalated regions. This clustering is probably favored at lower concentration. This paper demonstrates the possibility to study the local aspects of *in situ* intercalation, which opens promising opportunities to follow the formation and modifications of CDW's.

We want to thank F. Lévy for providing the VSe_2 samples and the staff at MAX-lab for their skillful assistance. This work was supported by the Swedish Natural Science Council.

---

[1] R. H. Friend, D. Jerome, D. M. Schleich, and P. Molinie, Solid State Commun. **27**, 169 (1978).

[2] H. P. Hughes, C. Webb, and P. M. Williams, J. Phys. C **12**, L173 (1979).

[3] M. T. Johnson, H. I. Starnberg, and H. P. Hughes, J. Phys. C **19**, L451 (1986).

[4] R. Manzke, O. Anderson, and M. Skibowski, J. Phys. C **21**, 2399 (1988).

[5] R. Coehoorn, A. A. van Heuzen, C. Haas, and G. A. Sawatzky, *Festkörperprobleme: Advances in Solid State Physics* (Academic, New York, 1985), Vol. XXV, p. 459.

[6] C. Pettenkofer, W. Jaegermann, A. Schellenberger, E. Holub-Krappe, C. A. Papageorgopoulos, M. Kamaratos, and A. Papageorgopoulos, Solid State Commun. **84**, 921 (1992).

[7] H. I. Starnberg, H. E. Brauer, L. J. Holleboom, and H. P. Hughes, Phys. Rev. Lett. **70**, 3111 (1993).

[8] R. V. Coleman, B. Giambattista, P. K. Hansma, A. Johnson, W. W. McNairy, and C. G. Slough, Adv. Phys. **37**, 559 (1988).

[9] B. Giambattista, C. G. Slough, W. W. McNairy, and R. V. Coleman, Phys. Rev. B **41**, 10 082 (1990).

[10] M. Remskar, V. Marinkovic, A. Prodan, and Z. Skraba, Surf. Sci. **324**, L367 (1995).

[11] M. Remskar, V. Marinkovic, and A. Prodan, Surf. Sci. **352/354**, 1012 (1996).

[12] H. E. Brauer, H. I. Starnberg, L. J. Holleboom, and H. P. Hughes, J. Phys. Condens. Matter **7**, 7741 (1995).

[13] H. E. Brauer, H. I. Starnberg, L. J. Holleboom, and H. P. Hughes, Surf. Sci. **331-333**, 419 (1995).

[14] H. E. Brauer, H. I. Starnberg, L. J. Holleboom, and H. P. Hughes, Surf. Sci. **357-358**, 345 (1996).

[15] H. E. Brauer, H. I. Starnberg, L. J. Holleboom, and H. P. Hughes (unpublished).

[16] D. Tang, D. McIlroy, X. Shi, C. Su, and D. Heskett, Surf. Sci. Lett. **255**, L497 (1991).

[17] I. Ekvall, Licentiate thesis, Chalmers University of Technology, 1997.

[18] C. Pettenkofer and W. Jaegermann, Phys. Rev. B **50**, 8816 (1994).

[19] S. Aminpirooz, L. Becker, H. Rossner, A. Schellenberger, and E. Holub-Krappe, Surf. Sci. **331-333**, 501 (1995).

[20] H. E. Brauer, H. I. Starnberg, L. J. Holleboom, V. N. Strocov, and H. P. Hughes (unpublished).

[21] S. Doniach and M. Sunjic, J. Phys. C **3**, 285 (1970).

[22] G. K. Wertheim and S. Hüfner, Phys. Rev. Lett. **35**, 53 (1975).

[23] J. Yeh, and I. Lindau, At. Data Nucl. Data Tables **32**, 1 (1985).

[24] G. A. Wiegers, Physica B **99**, 151 (1980).