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Exotic Atoms in Condensed Matter

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Proceedings of the Erice Workshop
at the Ettore Majorana Centre for Scientific Culture,
Erice, Italy, May 19 – 25, 1990

With 142 Figures

Springer-Verlag
Berlin Heidelberg New York
London Paris Tokyo
Hong Kong Barcelona
Budapest

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Preface

The topics of the fifth course of the International School of Physics of Exotic Atoms, which took place at the "Ettore Majorana" Centre for Scientific Culture, Erice, in Spring 1989, were the electromagnetic cascade and the chemistry of exotic atoms. The observed and reported influences of chemical structures on the formation and deexcitation mechanisms of exotic atoms suggested to G. Torelli, the Director of the School, the idea of an interdisciplinary workshop, where condensed matter physicists and exotic-atom specialists would have the opportunity to meet and to exchange views and information.

To bring people to an effective interdisciplinarity is not easy. Everyone feels generally more comfortable among specialists of his own domain. In this workshop, we had the luck that the specialists of either domain had a real interest in the other domain. Nobody expected to return to his home institution with a recipe for an interdisciplinary miracle. Everybody knows that it takes time, even if one starts early. This workshop intended to be such a start.

High-T_C superconductors and muon catalyzed fusion do not seem to have a lot in common. Through the talks of the various speakers, one gets, however, finally the impression that one can throw a bridge between these two fields and that the building of the bridge might become more important than the bridge itself.

The high intensity facilities for slow muons that seem likely to be constructed in the next decade have the potential to increase the maximum available flux by nearly three orders of magnitude. Such an increase should usher in a new era in cold muon studies of condensed matter. Their interaction with electrons promises new progress in core and deep level spectroscopies, hyperfine field analyses and spin-polarization spectroscopies of magnetic materials, polymers and high-T_C superconductors.

New impetus is expected for muon catalyzed fusion in solid hydrogen. Progress in this area, aiming at alternative fusion energy sources, has been envisaged as theoretically possible in high-density metallic deuterium. Fascinating alternatives in low-energy fusion, e.g., cluster fusion, are also discussed.

This book constitutes the proceedings of the Erice Workshop on Exotic Atoms in Condensed Matter, which was held at the "Ettore Majorana" Centre for Scientific Culture, between 19 and 25 May 1990. It reviews the state of the art in this domain of research, from meson factories and facilities to the basic interactions of muons and pions in condensed matter. It covers the applications and perspectives of muon- and pion-based analyses of solid state structural,

magnetic and superconducting properties. Some basic aspects of condensed matter physics which may be enlightened by exotic atoms spectroscopies are reviewed, together with applications to new sophisticated methods of chemical analysis. A section is devoted to muon catalyzed fusion in metallic deuterium.

The Workshop was jointly organized by the International School of Physics of Exotic Atoms and the International School of Physics of Solids under the auspices of the European Physical Society and the Regional Office for Science and Technology in Europe of UNESCO. It was sponsored by the Italian Ministry of Education, the Italian Ministry of University, Scientific and Technological Research, the National Research Council (CNR), the National Agency for Alternative Energies (ENEA), the Physics Department of the University of Milano and the Sicilian Regional Government.

The Ettore Majorana Centre for Scientific Culture was a very efficient pleasant host for this workshop, and our sincere thanks go to its Director, Antonio Zichichi, and to all the Centre staff.

Milan, Fribourg   G. Beneu
March 1991   H. Schneuwi

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Exotic Atom Formation
and Experimental Techniques

Solid State Effects in Atomic Capture of Negative Muons

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Abstract. The formation mechanism of exotic atoms is not yet well known. The muonic x-ray intensity patterns are, however, found to be sensitive to solid state structures, showing that the muon capture mechanism is influenced by the spatial distribution of bonding electrons. In compounds, pion and muon capture ratios are both influenced by the bond structure. Hydrogen compounds are cases of particular interest.

A negative muon is decelerated in a gas essentially through inelastic collisions with the atoms or molecules of that gas. When it has a sufficiently low kinetic energy, it is captured into the Coulomb field of an atomic nucleus. This capture process is not well known. One imagines that the muon loses its energy by ejecting an electron, and takes, in a certain sense, its place. Therefore, the muon is, at first, in an excited state and deexcites through Auger electron ejection and radiative transitions in a cascade finally to the ground state. These radiative transitions of energies characteristic to each element can easily be measured and their intensities can give information about the capture and cascade processes.

The intensities of muonic x-rays have been measured in argon gas at various pressures [1-4]. As may be seen from Table 1, the relative intensities of the Lyman series change with pressure. This change is due to the slower refilling of the electron shells, depopulated during the muonic cascade, at lower pressure. Indeed, the measured intensities can be reproduced by a muon cascade calculation [5] in all three cases by assuming an initial statistical

Table 1: Measured muonic x-ray intensities of the Lyman series in argon and reproduction of the muonic cascade with a statistical initial angular momentum distribution at n = 14. P_L is the population of the electronic L-shell used in the cascade calculation.

	Expt. 1.4 bar	Calc. P_L=2%	Expt. 22 bar	Calc. P_L= 3.5%	Expt. 170 bar	Calc. P_L=15%
2p-1s	.914(26)	.909	.905(25)	.899	.875(24)	.870
3p-1s	.0400(22)	.0395	.0410(14)	.0427	.0537(16)	.0509
4p-1s	.0097(11)	.0112	.0116(8)	.0128	.0187(8)	.0185
5p-1s	.0083(8)	.0066	.0095(6)	.0085	.0154(6)	.0161
6p-1s	(.0080)	.0065	(.0094)	.0086	(.0133)	.0155
7p-1s	.0077(8)	.0075	.0093(6)	.0090	.0111(15)	.0119

angular momentum distribution P(l) $\propto$ (2l + 1) in a level of main quantum number n = 14, and by adjusting the population of the electronic L-shell or, equivalently, the K-shell refilling width.

The observations made in argon gas is confirmed in neon. That the measured intensities can, in both elements, be reproduced by assuming a statistical angular momentum distribution, is of particular interest. Indeed, the muon capture process being insufficiently known, one can predict neither the orbit n of the capture level nor the angular momentum state l. One knows from quasi-classical approximations that, for muons cascading down from high n levels (n = 30-40), the angular momentum distribution remains practically unchanged, i.e. if the distribution is statistical in a high n level, it remains statistical down to levels of about n = 14. This means that in noble gases like neon and argon, the initial angular momentum distribution of captured muons is statistical.

At first sight, this statistical angular momentum distribution should reflect a spherical symmetry. If the muon capture proceeds through electron ejection, this distribution should be an image of the spatial symmetry of those electrons through which muons are captured.

In neon and argon, all electron shells are of spherical symmetry. However, in a one-to-one mixture of neon and argon, the ratio of muons captured in neon to those captured in argon has been measured to be A(Ne/Ar) = 1.01(3) [2], which indicates that the electrons do not all have the same weight in the capture process [6].

If the initial angular momentum distribution reflects the spherical symmetry of the electrons through which muons are captured, one expects that, when captured in Cl^- and K^+ ions, the muons have the same initial statistical angular momentum distribution. This is what is actually observed [3,4].

There is no reason to exclude muon capture through ejection of bonding electrons. In the case of silicon or diamond, where the spatial structure of the bonding electrons is essentially given by hybridization of the $3sp^3$ or $2sp^3$ orbitals, the symmetry is the same as that of full atomic (3s,3p) or (2s,2p) shells, respectively. One would, therefore, not be surprised to reproduce the muonic x-ray intensities measured in silicon and diamond by a cascade calculation assuming again a statistical initial angular momentum distribution. The measured muonic x-ray intensity structures in silicon and diamond are, indeed, reproduced by such a statistical distribution [4,7,8]. In addition, the muonic x-ray intensity pattern measured in nitrogen of cubic boron nitride, where the spatial electronic structure is comparable to diamond, can also be reproduced with the same distribution [8].

In graphite and in nitrogen of hexagonal boron nitride, the muonic x-ray intensity structures are different [8], showing a clear solid state effect. They can only be reproduced by assuming a greater population of lower angular momentum states. The difference in the angular momentum population may be attributed in both cases to a different symmmetry in the spatial distribution of the bonding electrons [9]. In the diamond structures one has four σ-bonds and in the hexagonal structures one of the four bonds is a delocalized π-bond.

In addition to the differences observed in the muonic x-ray intensity structures in nitrogen between cubic and hexagonal boron nitride, one has also found a significant difference in the atomic muon capture ratios A(B/N)

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between the two allotropies. This difference is explained in terms of differences in B-N bond dipole moments, expressed through bond ionicities [8], and its explanation is consistent with the one given for the muonic x-ray intensity structures.

These observations and their explanation stimulate our confidence in the understanding of the main mechanism of muon capture.

In the ions F^- and Na^+, which have the same electronic structure as neon, one expects that the captured muons have also a statistical initial angular momentum distribution. The muonic x-ray intensities have been measured in these elements in the ionic compounds KF and NaCl, where both K^+ and Cl^- showed a statistical muon distribution. The muonic fluorine x-ray intensities can, indeed, be reproduced by assuming a statistical initial angular momentum distribution, whereas those of sodium cannot. The pattern of the muonic sodium x-rays measured in NaCl is not a special case. In a whole series of compounds, where sodium can, in good approximation, be considered as an ion, the muonic sodium x-ray intensities are the same [10,11]. Even metallic sodium has the same pattern [11]. From this last observation one deduces that the electron refilling in a conductor does not be measurably different from the refilling in insulators.

The difference between the muonic sodium x-ray intensity pattern and those measured in the other isoelectronic elements of neon and argon may be related to different weights of the electronic shells and subshells in muon capture. Indeed, one might expect that the per atom capture ratio A(Na/Cl) measured in NaCl were equal to the capture ratio A(Ne/Ar). One does not expect that muon capture ratios like A(K/Cl), A(Na/F) and A(Na/Cl), measured in KCl, NaF and NaCl are exactly equal to unity, because the bonds are not ideally ionic. For the first two ratios, the mean values A(K/Cl) = 1.15(5) and A(Na/F) = 0.96(5) are near to unity, but A(Na/Cl) = 0.73(5) indicates that about 25% less muons are captured by sodium than by chlorine. By assuming that only electrons with binding energies less than $E = 60$ eV participate in muon capture, the measured A(Na/Cl) capture ratio can be reproduced [6].

The inital statistical angular momentum distribution of captured muons observed in the other elements is then explained by capture via the electrons of the outermost full s- and p-shells. The capture in sodium would then proceed only via the six electrons of the 2p shell [3,4,6]. This approach, even if it explains these and a lot of other muon capture data [12], does not account for the capture ratios A(K/F) and A(Na/F) measured in KF and NaF. The present model [6] would predict about 1.0, resp. 0.75, and the measured values are 1.89(18), resp. 0.96(5).

Solid state effects are not only observed in the muonic x-ray intensity structures of carbon and of nitrogen in boron nitride between hexagonal and cubic structures, but also in those of selenium between the metallic and amorphous allotropies [13]. In phosphorus, differences have been found between the white modification and the red and black ones, but no difference between the last two (Fig. 1) [13].

Pions are also very sensitive to the chemical bond as has been shown by Imanishi et al. [14,15]. They have measured the pion capture in boron compounds and corresponding mechanical mixtures. The differences in the per atom capture ratios between the compounds and the mechanical mixtures range from a factor of two to seven. Different chemical bonds in beryllium borides
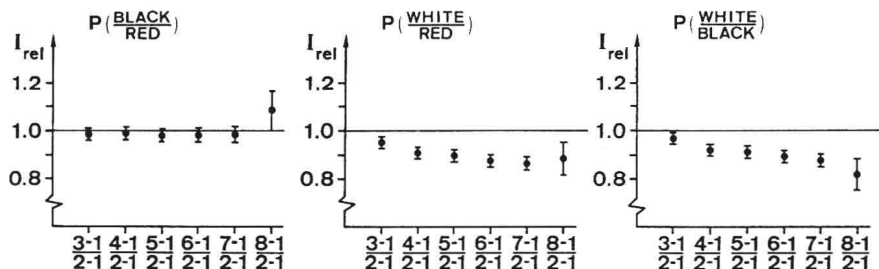
Figure 1: Relative muonic x-ray intensity ratios of the Lyman series for the three phosphorus modifications : white, red and black.

Table 2: Experimental atomic (per atom) Coulomb capture ratios of negative pions, A(Z/B), for compounds and mechanical mixtures of boron with beryllium and carbon.

Elements	x/y	$xB + yZ$	B_xZ_y	$(xB+yZ)/B_xZ_y$
B and Be	1/4	0.76(2)	0.40(2)	1.9
B and Be	1/2	0.75(3)	0.36(2)	2.1
B and Be	2/1	0.73(2)	0.25(2)	2.9
B and Be	6/1	0.75(5)	0.10(3)	7.1
B and C	4/1	0.78(12)	0.55(6)	1.4

change the per atom capture ratios A(Be/B) by up to a factor of four (Table 2). Measurements of pion capture in LiF, NaF and KF show that the pion capture ratios A(M/F) are identical to the corresponding muon capture ratios [16].

The muon capture in NaCl and $NaClO_2$, $NaClO_3$, $NaClO_4$ has been investigated in great details [17]. The muonic x-ray intensity structures of oxygen are identical in all three oxygen containing compounds. The same proves true for the chlorine x-rays. The only difference observed has been in chlorine between NaCl and the $NaClO_x$ compounds, where the relative intensities of the Lyman series change by up to 50%. The muonic x-ray pattern in sodium is the same in all four compounds, which presents no surprise, the sodium bond being in all four compounds highly ionic.

Surprising is, however, that the atomic muon capture ratio A(Na/Cl) is practically the same in NaCl and in the $NaClO_x$ compounds and that the A(Cl/O) capture ratio (per atom) decreases with increasing oxygen content (Fig. 2). The measured muon capture ratios A(Na/Cl) and $A(ClO_x/Na)$ agree nicely with model predictions (Table 3). The A(Cl/O) and A(Na/O) capture ratios can only be reproduced by model calculations if one assumes that the Cl-O bond dipole moments or, equivalently, the ionicity of the Cl-O bonds are different in the three compounds.

In empirical intensity correlations in muonic x-ray spectra of oxides, Daniel et al. [18] found a weak correlation, e.g., between the muonic K_α intensity in oxygen and the Pauling ionicity of the oxygen bond. They found a strong correlation between the atomic radii and the ionicity.
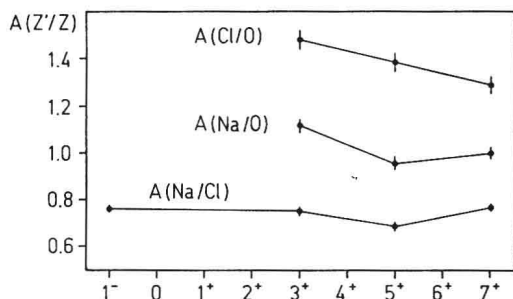
Figure 2: Per atom muon capture ratios A(Cl/O), A(Na/O) and A(Na/Cl) measured in $NaClO_2$, $NaClO_3$, $NaClO_4$ and NaCl as a function of the formal chlorine valency.

Table 3: Comparison of measured muon capture ratios $A(ClO_x/Na)$ in NaCl, $NaClO_2$, $NaClO_3$ and $NaClO_4$ with model predictions [6].

	NaCl	$NaClO_2$	$NaClO_3$	$NaClO_4$
Experiment [17]	1.32(3)	3.13(7)	4.56(11)	5.32(12)
Model [6]	1.32	3.33	4.33	5.33

Figure 3 displays the muonic K_β/K_α intensity ratios of oxygen measured in oxides of the third row elements [19] in dependence of the Pauling ionicities defined through the electronegativities of the elements. At first glance, the correlation is not obvious unless one were guided by the broken line, drawn to suggest the correlation. However, the oxygen bond in Na_2O_2 has not the ionicity of a Na-O bond ($\sigma=82\%$) because, naively speaking, one oxygen atom is also bound to the other such that the mean ionicity of the oxygen bond is about 40 to 50%. Then the correlation is plausible.

Following our model [6] in its simplest version, the capture into oxygen should proceed through four core L-electrons on one side and partly through the two pairs of binding electrons on the other side, the part being determined through the bond ionicity and the nuclear charges of the bond partners. In a highly ionic compound like MgO ($\sigma=73\%$), 43% of the muons reaching the 1s state in oxygen are assumed to be captured via the binding electron pairs, compared to 28% in P_2O_5 ($\sigma=39\%$). In oxygen of the oxides of the third row elements, this percentage increases with increasing ionicity, whereas the muonic K_β/K_α intensity ratio decreases.

A similar but much less pronounced trend is observed in chlorine of corresponding compounds of elements of the same row (Fig. 4). The K_β/K_α intensity ratios seem, however, much less sensitive to the change in ionicity, whereas the higher transitions show a clear decrease in intensity [20]. The explanation for the observed trend is analogous to that for the oxides [21].

The proposed explanation for the decrease of the muonic K_β/K_α intensity ratios in oxygen and chlorine of third row compounds with increasing ionicity cannot be simply extended to other compounds. Indeed, in boron nitride in cubic and hexagonal structures, one had to assume different bond
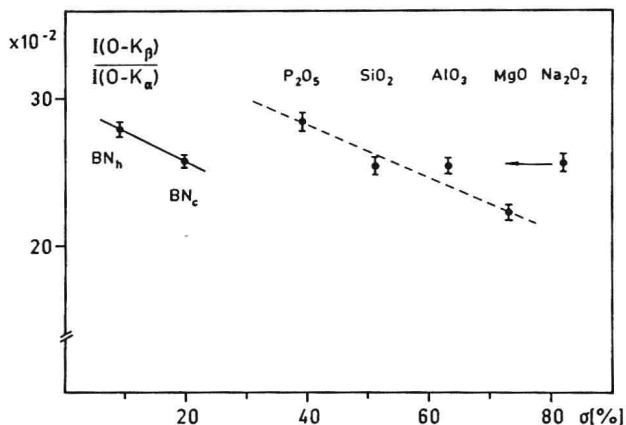
Figure 3: Muonic K_β/K_α intensity ratios in oxygen of oxides of third row elements as a function of bond ionicities. Muonic K_β/K_α intensity ratios in nitrogen of boron nitride in hexagonal (BN_h) and cubic (BN_c) structures are also shown. The lines are only drawn to guide the eye.
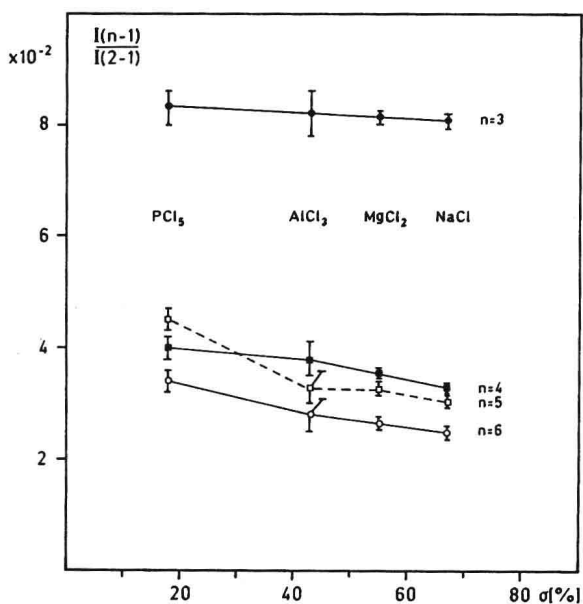

Figure 4: Muonic $I(n-1)/I(2-1)$ intensity ratios ($n=3,4,5,6$) in chlorine of chlorides of third row elements as a function of the bond ionicities. The lines are drawn to guide the eye.
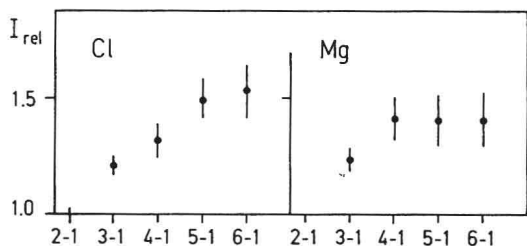
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Figure 5: Muonic Lyman series intensities of chlorine and magnesium, normalized to the respective K_α intensities, in 4M relative to those of anhydrous $MgCl_2$.

ionicities in order to reproduce with our model the measured A(B/N) muon capture ratios. The muonic nitrogen K_β/K_α intensitiy ratios in the two structures of boron nitride agree with the trend observed in oxygen (Fig. 3).

However, these K_β/K_α intensity ratios in the two structures can be explained independently from the ionicity like in carbon,in diamond and graphitic structures [9]. Another example are the muonic K_β/K_α intensity ratios in oxygen of Cr_2O_3 and CrO_3 [22]. The ionicity of the Cr-O bond is greater in Cr_2O_3 than in CrO_3. The oxygen intensity ratio increases with increasing ionicity, which is opposite to the trend observed in the oxides of third row elements. However, in chromium compounds like in iron compounds d-electrons are involved in the bonds, whereas third row elements have only s- and p-electrons. The observed trends represented in Figs. 3 and 4 might well be related to the fact that the bond partners contribute only through s and p electrons to the bonds to oxygen and chlorine.

The observed correlations to the bond ionicities confirm the dominant role played by the outer electrons of the bond partners in atomic muon capture.

As already shown, the initial angular momentum distribution of muons captured by Cl- is statistical as for argon. For muons which are transferred to argon from muonic hydrogen atoms, this angular momentum distribution is strongly peaked to low angular momenta [23]. The resulting muonic x-ray intensity pattern is, consequently, also different. In particular, the intensities of the higher members of the Lymans series are strongly enhanced.

In an experiment, Daniel et al. [24] have compared the muonic x-ray intensity patterns in magnesium and chlorine in crystalline $MgCl_2$ to those measured in a 4M solution. (Fig. 5). From the strong enhancements of the intensities of the higher members of the Lyman series in both elements, they concluded that muon transfer is responsible for the observed hydrogen effects while mechanisms involving muon-molecular orbitals are ruled out.

In a similar experiment, we have investigated the muonic x-ray intensities in calcium and chlorine in $CaCl_2$ anhydride and in $CaCl_2 \cdot 2H_2O$ and $CaCl_2 \cdot 4H_2O$. In chlorine, the observed differences in the intensities are correlated to the quantity of water of crystallization. In calcium, the enhancement of the intensities due to the presence of hydrogen is hardly visible (Fig. 6). If the enhancement of the muonic x-ray intensities were essentially due to muon transfer from the ground state of muonic hydrogen atoms, one would expect that the enhancements were approximately the same in both elements as was the case in $MgCl_2$. If the enhancement were due to transfer from excited μp^*
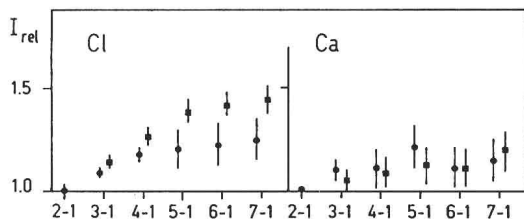
Figure 6: Muonic Lyman series intensities in chlorine and calcium, normalized to the respective K_α intensities, in $CaCl_2 \cdot 2H_2O$ (circles) and in $CaCl_2 \cdot 4H_2O$ (squares) relative to anhydrous $CaCl_2$.

states, then the cations should even be favoured [25]. By comparing the per atom capture ratios A(Ca/Cl) in $CaCl_2$ anhydride to those in the water containing samples:

$$\frac{A(Ca/Cl) \text{ anhydride}}{A(Ca/Cl) \text{ in } CaCl_2 \cdot 2H_2O} = 1.036(18)$$

$$\frac{A(Ca/Cl) \text{ anhydride}}{A(Ca/Cl) \text{ in } CaCl_2 \cdot 4H_2O} = 1.079(18)$$

one observes that capture in chlorine is increased with increasing water content as suggested by the muonic x-ray patterns.

The observed intensity enhancements can, therefore, not be explained through muon transfer alone. Actually, comparable enhancements have been observed in elements bound to hydrogen compared to the pure element or other compounds, i.e., the hydrogen bond has a particularly strong influence on the initial angular momentum distribution of captured muons.

There are already a lot of experimental data on muon capture available. Some systematic investigations have been performed. Some understanding of the capture machanism has been achieved. No model seems, however, exempt from contradictions with experimental results. Further effort has to be made to increase our knowledge on the atomic capture of muons and pions in mixtures of elements and compounds. Combined analyses of muonic x-ray structures and muon capture ratios seem to be a promising way. New ideas seem, however, necessary to make decisive progress in the understanding of the atomic capture mechanism.

References

1. J.D. Knight, C.J. Orth, M.E. Schillaci, R.A. Naumann, F.J. Hartmann and H. Schneuwly, Phys. Rev. A **27**, 2936 (1983).
2. P. Ehrhart, F.J. Hartmann, E. Köhler and H. Daniel, Z. Physik **A311**, 259 (1983).
3. R. Jacot-Guillarmod, F. Bienz, M. Boschung, C. Piller, L.A. Schaller, L. Schellenberg, H. Schneuwly and D. Siradovic, Phys. Rev. A **37**, 3795 (1988).