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Giant Resonance Enhancement of the 4f, 5p and 5s States in the Photoemission Spectra of Rare Earth Compounds

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Abstract

We have measured photoemission from the valence band and outer core levels of rare earth (Ce, Gd, La) penta-phosphates. Varying the photon energy through the region of the giant resonance of the 4d cross section (hν = 100 eV - 200 eV), we find a dramatic enhancement of the rare earth derived states (4f, 5p, 5s) in the EDC's. This enhancement is explained as being due to a strong interaction of the $4d^9 4f^{n+1}$ *configuration with other configurations as e.g.* $4d^{10} 4f^{n-1} \varepsilon \ell$ *(autoionization).*

The absorption spectra of the solids containing rare earth (RE) elements are characterized by a large broad maximum in the energy region 10 - 20 eV above the RE 4d ionization threshold.[1-3] The energy position of this maximum varies between ∿ 120 and ∿ 190 eV when following the series of RE metals from La to Yb while it has completely disappeared in the spectrum of Lu. Although 4d ionization is possible at these photon energies,[4] the excitation of this maximum, its correlation and systematic variation in shape and strength with the availability of empty 4f states lead to an interpretation as a $4d^{10}4f^n \rightarrow 4d^9 4f^{n+1}$ transition. The extremely strong multiplet splitting of the $4d^9 4f^{n+1}$ configuration due to the exchange interaction of strongly overlapping wavefunctions of two incomplete shells pushes the strongest lines of this multiplet to energies way above the lowest ionization threshold. The autoionization decay of the $4d^9 4f^{n+1}$ configuration into the $4d^9 4f^n \varepsilon f$ configuration is held responsible for the broadening of these multiplet lines.[5-8]

Up to now, the region of these maxima was investigated by absorption spectroscopy,[1-3] and by fluorescence emission spectroscopy.[9] We present here for the first time measurements using the technique of photoelectric emission with variable photon energy. This method yields a better insight into the mechanisms leading to these peaks. From our results we conclude that in addition to the decay mode proposed by Dehmer et al.[5] a strong autoionization of the $4d^9 4f^{n+1} 5s^2 5p^6$ configuration into the following free electron configurations occurs: $4d^{10} 4f^n 5s^1 5p^6 \varepsilon \ell$, $4d^{10} 4f^n 5s^2 5p^5 \varepsilon \ell$, and $4d^{10} 4f^{n-1} 5s^2 5p^6 \varepsilon \ell$. We observe these configurations directly in photoemission by analyzing the $\varepsilon \ell$ electron and we can see a pronounced enhancement of these states in the region of the 4d maximum.

In this paper we report on EDC measurements of RE penta-phosphates, namely CeP_5O_{14}, $Gd_{0.67}La_{0.33}P_5O_{14}$. These compounds have become famous by the first high concentrated RE laser material Nd P_5O_{14},[10] containing the Nd^{3+} ion as a stoichiometric constituent. The existing spectroscopic investigations of the RE P_5O_{14}'s are restricted to transitions within the 4f-subshell, as these transitions are of main interest when developing optical devices, like solid state lasers. However, a deeper understanding of the nature of 4f-transition probability and of the interaction mechanisms between the different ions in these crystals necessitates a precise knowledge of how the RE 4f-levels are embedded within the other states. The measured EDC's yield information in this context and our results may contribute to understand some of the basic problems of stoichiometric laser materials.[11]

Using synchrotron radiation in the range 60 to 200 eV we have studied the photoemission of the valence band and outer core levels of CeP_5O_{14} and $GdLaP_5O_{14}$. Our investigations take special advantage of the yield spectroscopy technique which gives information of the spectral dependence of the optical absorption. We observe a strong resonance enhancement of the rare earth derived states for photon energies in the region of the RE 4d transitions.

Experimental

The measurements were performed monochromatizing the synchrotron radiation of the DORIS storage ring by the FLIPPER-monochromator.[12] The photoelectrons were excited with s-polarized light and analysed with a commercial double pass cylindrical mirror analyzer operating at a fixed energy resolution. An overall resolution of about 0.5 eV was sufficient for resolving the structures in the EDC's. The yield spectra were taken setting the energy analyzer to a fixed kinetic energy of 10 eV with a band pass of 0.12 eV.

The samples were crystals grown from the stoichiometric melt. They were placed as grown with the (100) surface into the vacuum system evacuated to $\sim 10^{-8}$ Torr. Since our crystals are fairly good insulators ($E_{gap} \gtrsim 7 - 8$ eV[13]) we have used a flood gun for charge compensation.

Results and Discussion

Fig. 1 shows a set of EDC's of CeP_5O_{14} taken a different photon energies. The spectra are plotted on a binding energy scale with the zero corresponding to the top of the valence band. The positions of peaks in the EDC's of insulators can be shifted by charging effects which prevent an absolute determination of the binding energy. Nevertheless the relative peak positions are hardly affected. Due to the high oxidation state of the P ion (P^{5+}) in this compound only RE- and O-states contribute to the EDC-spectra in this energy range. The identified states are assigned in Fig. 1 according to Refs. 4, 14. We emphasize the dramatic variation of the intensity of the Ce^{3+} derived states (4f, 5p, 5s) with photon energy. Especially at photon energies around 120 eV the Ce 4f peak shows a significant enhancement.

Analogously to Fig. 1,Fig. 2 b shows EDC's of $Gd_{0.67}La_{0.33}P_5O_{14}$ at different photon energies. Again we observe a strong dependence of structures in the spectra on the photon energy: (i) A photon energy of hν = 118 eV gives rise to additional structures at binding energies around 16 eV and 35 eV. (ii) Around hν = 150 eV a dominant peak appears in the valence band region.

It is well-known that the Ce 4d transitions cause a giant resonance near $h\nu$ = 120 eV in the absorption spectra of Ce metal and Ce compounds. Fig. 3 shows the yield spectrum[15] of CeP_5O_{14}. The strong increase of the yield near 120 eV is due to the Ce 4d transitions. In Fig. 3 the measured photoyield is compared to the absorption coefficient of Ce metal.[2] One has to consider that in the compound a flat background due to excitations from the matrix contributes to the spectrum. In the energy range 110 - 135 eV both spectra, yield and absorption, have a nearly identical shape, which again prooves the atomic character of the 4d transitions in the RE solids.[16] The features observed at about 138 eV in the yield spectrum are ascribed to 2p excitations of the P^{5+} ion.

The results of our EDC measurements (Fig. 1) suggest a correlation between the observed enhancement of the 5s, 5p and 4f states of Ce^{3+} and the 4d-excitation. The intensities of the Ce 4f, 5p and 5s peaks as determined from the EDC's are plotted in Fig. 3. From Fig. 3 it is evident that the strong increase of the intensities of the RE-derived states is correlated with the onset of the Ce giant resonance absorption. This resonance behaviour can be interpreted by autoionization of the excited $4d^9 4f^2 5s^2 5p^6$ states via $4d^{10} 4f^0 5s^2 5p^6 + \varepsilon\ell$, $4d^{10} 4f^1 5s^2 5p^5 + \varepsilon\ell$, and $4d^{10} 4f^1 5s^1 5p^6 + \varepsilon\ell$ configurations.

Similarly West et al.[17] have found an increase of the partial photo-ionization cross sections for 5s- and 5p-excitations in Xe above the threshold of 4d-transitions due to intershell interactions. In theoretical calculations of the Ce 4d-transitions the $4d^9 4f^1 5s^2 5p^6 + \varepsilon f$ configurations are assumed to be the main autoionization channels. This process leads to free electrons with low kinetic energy. These electrons cannot be identified in our EDC measurements because of the high background of scattered electrons and the additional slow electrons emitted by the flood gun. We were able, however, to estimate the relative contribution of the autoionization channels observed in the EDC's.

Our evaluations are carried out at a photon energy of $h\nu$ = 121.6 eV at which we obtained maximum intensity for the Ce derived states in the corresponding EDC (Fig. 1). It was demonstrated[15] for practically all kinds of solids that the photoelectric yield γ is proportional to the absorption coefficient μ and the escape depth L of the photoelectrons, $\gamma \sim \mu L$ (if $1/L \gg \mu$). The yield at $h\nu$ = 121.6 eV can be split into a contribution due to the Ce 4d-excitation (b in Fig. 3) and another part due to the matrix excitation (a). From Fig. 3 follows a ratio of these contributions $R = b/a \approx \frac{\mu^{4d}}{\mu\ \mathrm{matrix}} = 2.2$ at $h\nu$ = 121.6 eV. The excitation of matrix derived states is reflected in the integrated intensity M of the valence band structure and the O^{2-} 2s peak in the EDC (Fig. 1). The area F under the 4f peak represents those Ce 4d-excitations leading to $4d^{10} 4f^0 5s^2 5p^6 + \varepsilon\ell$ final states. From Fig. 1 one obtains F/M = 0.3. In order to determine the relative contribution β^{4f} of the 4f-autoionization channel one has to correct this value by the ratio R. Thus it follows $\beta^{4f} = F/M \cdot 1/R = 0.13$. An analogous procedure is applied to the 5p and 5s peaks in the EDC yielding $\beta_{4f} + \beta_{5s} + \beta_{5p} = 0.20$. This means that the three observed autoionization channels give a 20 % contribution to the decay of the excited $4d^9 4f^2 5s^2 5p^6$ states at $h\nu$ = 121.6 eV. The $4d^{10} 4f^{n-1} \varepsilon\ell$ autoionization can be described as a super Coster-Kronig transition[18] involving interacting electrons with the same main quantum number. This may explain the particularly enhanced decay into this autoionization channel.

When making this analysis we have completely neglected direct - not resonance enhanced - 4f, 5p and 5s excitations of Ce. The comparison of the yield spectrum of CeP_5O_{14} with the absorption spectrum of metallic Ce (see Fig. 3) allows to estimate this contribution to the total error of the β-values to be 15 %. Considering the ambiguity of the background substraction in the EDC (Fig. 1) we estimate the total error to be ± 30 % of the β-values.

We emphasize that the maximum in the enhancement of the Ce derived states in the EDC spectra does not coincide with the maximum of the 4d absorption in Fig. 3. The strongest autoionization decay into these states occurs at the low energy part of the giant resonance. We have fitted the shape of these curves with a Fano autoionization profile[19] actually developed for one single resonance state overlapping one continuum. The fit is not too bad and the parameters obtained are given as following: E_o = 120.2 eV, Γ = 2.6 eV, q = 2.4 eV.

We have also measured the yield spectrum of $GdLaP_5O_{14}$ (Fig. 2 a). The prominent features around 118 eV and 147 eV are correlated with the giant resonances observed in the absorption spectra of La- and Gd-metal.[1] At photon energies corresponding to the 4d excitations of La^{3+} there is an obvious enhancement of the La 5s and 5p states in the EDC's (Fig. 2 b). The 4d-excitations of Gd peak at hν = 147 eV (Fig. 2 a). Therefore the strong structure rising in the valence band region at this photon energy is ascribed to Gd^{3+} 4f states. Keeping in mind that the 4f subshell of Gd is half-filled the position of the Gd 4f states with respect to the Ce 4f state supports this interpretation.

Conclusion

We could demonstrate in these measurements that the so called giant resonance maxima in the RE spectra above the 4d ionization limit arise from resonance like states of the $4d^9 4f^{n+1}$ type. Not only the previously postulated[5-8] $4d^9 4f^n \varepsilon f$ decay is responsible for the broadening of these states but also other autoionization decays mainly of the type $4d^{10} 4f^{n-1} \varepsilon \ell$ occur with a fairly high probability of up to 20 %. Such a decay channel is only possible for a well localized resonance like excitation for which it is a strong indication. The investigation of RE compounds rather than pure metals was very useful for establishing these effects. The phosphor and oxygen derived matrix states which are unaffected by these processes served as a good frame of reference for normalizing the intensities of the Ce derived peaks in the EDC spectra.

Moreover, the mechanism described above is very pronounced and easy to observe when a tunable synchrotron radiation light source is available. Therefore the RE derived states overlapping the valence band can be identified by this enhancement. In our measurements this leads to a localization of the 4f levels with respect to the valence band in CeP_4O_{14} and $GdLaP_5O_{14}$. The implications of these results will be discussed in detail in another paper.

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References

1. T.M. Zimkina, V.A. Fomichev, S.A. Gribovskii, and I.I. Zhukova, Sov. Phys.-Sol. State 9, 1128 (1967)
2. R. Haensel, P. Rabe,and B. Sonntag, Sol. State Commun. 8, 1845 (1970)
3. Shoji Suzuki, Takehiko Ishii, and Takasi Sagawa, J. Phys. Soc. Japan 38, 156 (1975)
4. S.P. Kowalczyk, Ph. D. Thesis, Burkley, LBL-4319 (1976)
5. J.L. Dehmer, A.F. Starace, U. Fano, J. Sugar, and J.W. Cooper, Phys. Rev. Lett. 26, 1521 (1971)
6. A.F. Starace, Phys. Rev. B5, 1773 (1972)
7. J. Sugar, Phys. Rev. B5, 1785 (1972)
8. J.L. Dehmer, and A.F. Starace, Phys. Rev. B5, 1792 (1972)
9. T.M. Zimkina, V.A. Fomichev, and S.A. Gribovskii, Sov. Phys.-Solid State 15, 1786 (1974)
10. H.G. Danielmeyer, and H.P. Weber, IEEE J. Quantum Electr. QE-8, 805 (1972)
11. H.G. Danielmeyer, Stoichiometric Laser Materials, in: Festkörperprobleme XV, H.J. Queisser (ed.), Pergamon/Vieweg, Braunschweig (1975)
12. W. Eberhardt, G. Kalkoffen, and C. Kunz, Nucl. Instrum. and Methods, in press
13. B. Blanzat, J.-P. Denis, and J. Loriers, Proc. Tenth Rare Earth Research Conference Vol. II, 1170 (1973)
14. S. Sato, Y. Sakisaka, and T. Matsukawa, Proc. 4th Int. Conf. on VUV Radiation Physics, Hamburg, eds. E.E. Koch, R. Haensel, and C. Kunz, Pergamon/Vieweg, Braunschweig (1974)
15. W. Gudat, and C. Kunz, Phys. Rev. Lett. 29, 169 (1972)
16. H.W. Wolff, R. Bruhn, K. Radler, and B. Sonntag, Phys. Lett. 59A, 67 (1976)
17. J.B. West, P.R. Woodruff, K. Codling, and R.G. Houlgate, J. Phys. B, Atom. Molec. Phys. 9, 407 (1976)

18. E.J. McGuire, J. Phys. Chem. Solids 33, 577 (1972)
19. U. Fano, Phys. Rev. 124, 1866 (1961)

Figure Captions

Fig. 1: Photoelectron EDC's of the valence band region for CeP_5O_{14} taken at different photon energies. The spectra are plotted on a binding energy scale with the top of the valence band $E_B = 0$. The curves are normalized at $E_B = 15$ eV.

Fig. 2: (a) Yield spectrum of $GdLaP_5O_{14}$

(b) Photoelectron EDC's of the valence band region for $GdLaP_5O_{14}$ measured at different photon energies (as indicated in Fig. 2 a). The spectra are plotted on a binding energy scale with the top of the valence band $E_B = 0$. The curves are normalized at $E_B = 12$ eV.

Fig. 3: Solid line: yield spectrum of CeP_5O_{14}, dashed line: 4d absorption of Ce metal (from Ref. 2), marks: amplitudes of Ce derived states from the EDC's in the vicinity of the Ce 4d giant resonance, dash-dotted line: autoionization profile according to Ref. 19 with the following parameters: $E_o = 120.2$ eV, $\Gamma = 2.6$ eV, $q = 2.4$ eV.

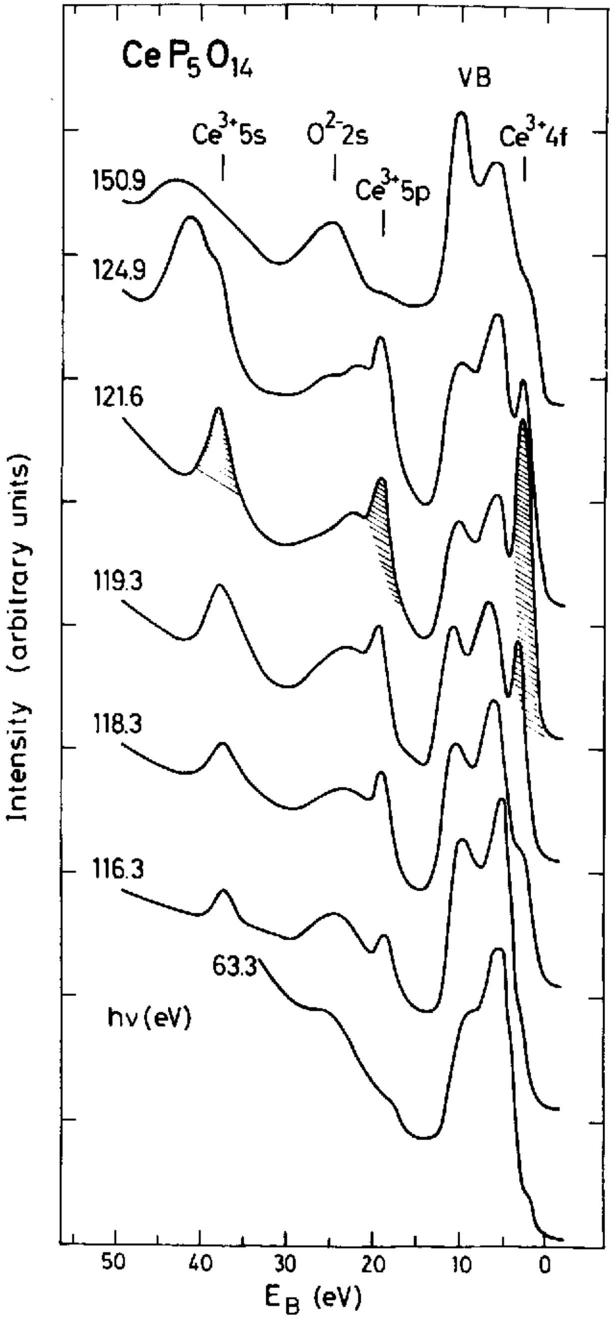

Fig. 1

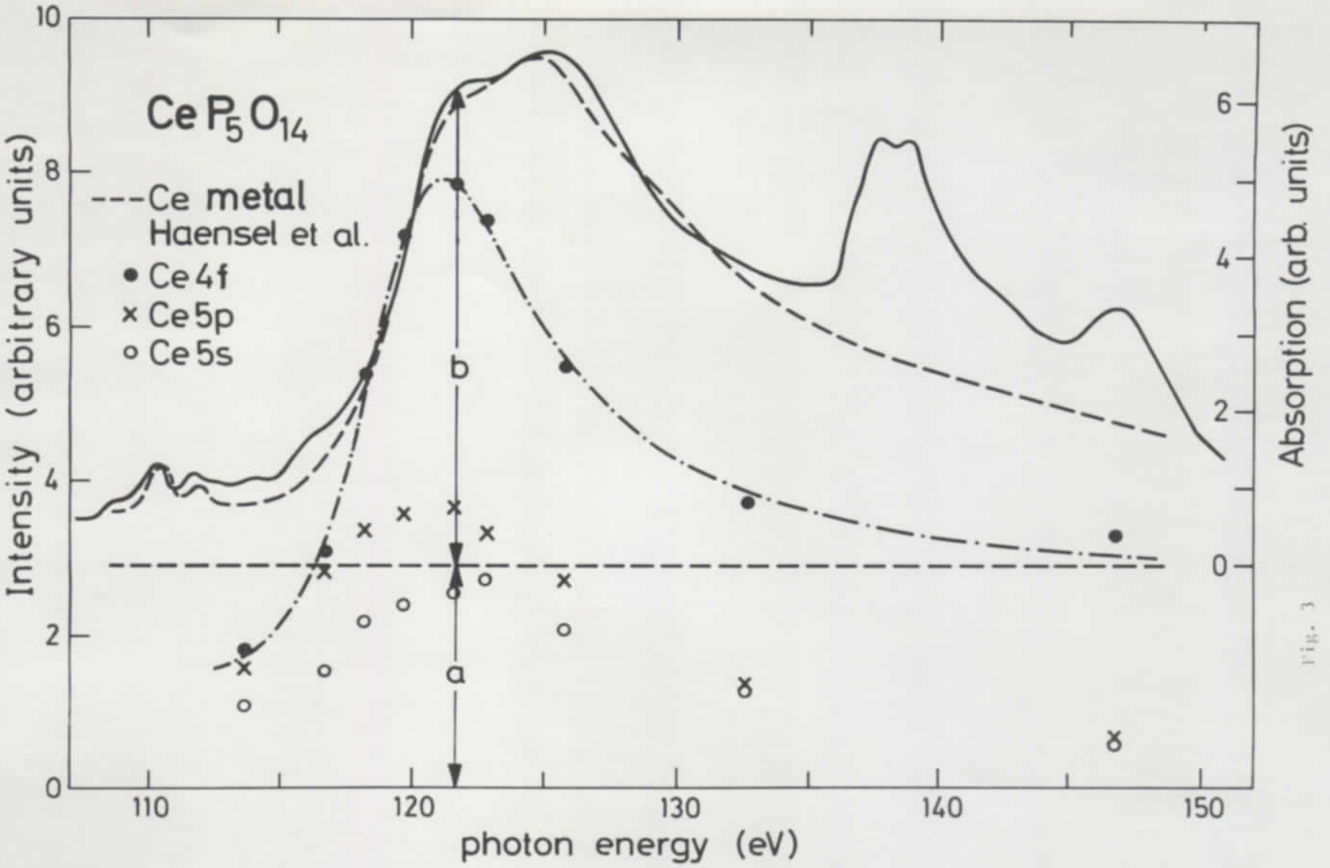
Ce P5 O14
---Ce metal
Haensel et al.
● Ce 4f
× Ce 5p
○ Ce 5s
b
a
Intensity (arbitrary units)
Absorption (arb. units)
photon energy (eV)
0
2
4
6
8
10
110
120
130
140
150

Fig. 3

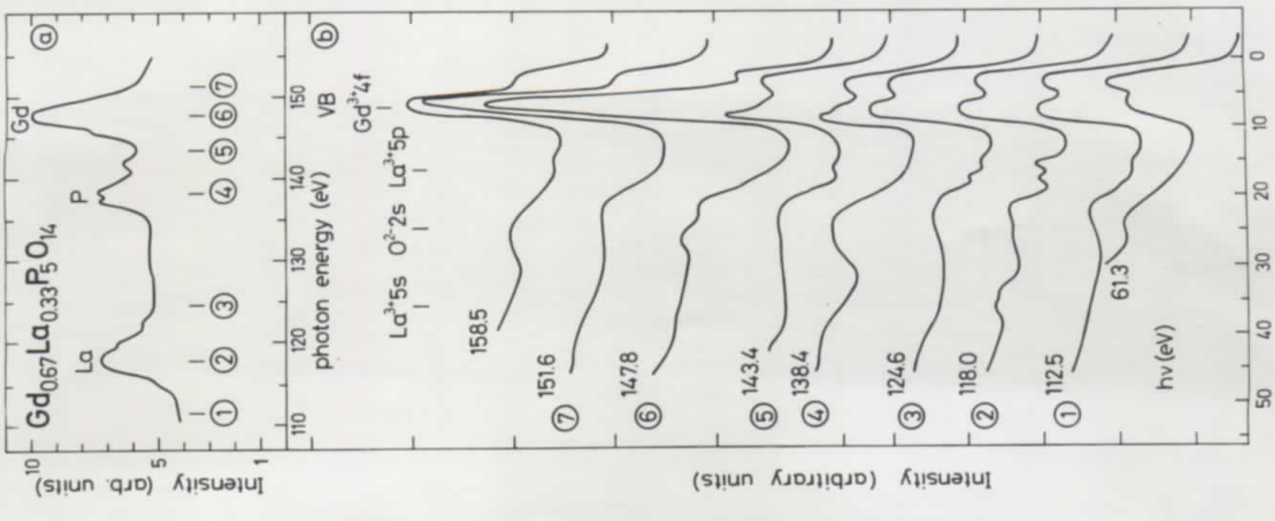
Gd0.67La0.33P5O14
a
b
La
P
Gd
Intensity (arb. units)
photon energy (eV)
110
120
130
140
150
① ② ③ ④ ⑤ ⑥ ⑦
VB
Gd3+4f
La3+5p
O2-2s
La3+5s
158.5
151.6
147.8
143.4
138.4
124.6
118.0
112.5
61.3
hv (eV)
E_B (eV)
0
10
20
30
40
50
Intensity (arbitrary units)

Fig. 2