MICROANALYSIS OF Si, S AND Zn IN GaSb BY USE OF DIRECT OBSERVATION OF (p, p'γ) REACTIONS

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The use of direct observation of nuclear reactions (p, p'γ) is discussed. The main characteristics of this method are presented and applied to the case of the microanalysis of Si, S and Zn in GaSb.

Introduction

This investigation has been undertaken upon the request of a Solid State Physics Laboratory whose work is mainly concerned with intermetallic semiconductors such as GaSb. In their studies a non-destructive method allowing the determination of the concentration profile would be very fruitful. We received samples doped with Zn and S. We thought that direct observation of nuclear reactions could be an interesting tool; we have chosen (p, p'γ) reactions which offer several advantages:

— in the case where the outgoing particles are photons, the absence of slowing down and straggling in the target allows a better energy resolution while the attenuation is quite negligible;

— the identification of the nucleus responsible for the γ-transition is not ambiguous due to the very good energy resolution of the detector (~6 keV), and consequently discrimination between the atoms of impurities and of the lattice matrix is possible even if their Z and A values are not too different;

— the cross-sections for (p, p'γ) reactions between 3 and 4 MeV reach considerable values and are increased, in the case of light atoms, by the existence of resonances.

These characteristics have been used for a quantitative evaluation of Si, S and Zn in GaSb, and especially to determine the limits of the sensitivity in this particular lattice. It is shown that the concentration profile of Si and S can easily be determined. A description is also given of the data processing, which makes possible an improvement of the sensitivity.

Principle

The reaction yield from which we evaluate the number of atoms contributing to the nuclear reactions is defined by the equation:

$$Y(E_p, t) = n \int\limits_{x=0}^{t} \int\limits_{E_i=0}^{\infty} \int\limits_{E=0}^{\infty} g(E_p, E_i) f(E_i, E, x) \, \sigma(E) \, dE \, dx \, dE_i \qquad (1)$$

where E_p — proton incident energy,

t — target thickness,

x — distance between the front face of the target and the position of the nucleus submitted to the nuclear reaction,

n — number of atoms per cm^3,

$g(E_p, E_i)dE_i$ — the probability for a proton of the incident beam to have its energy in an interval E_i, $E_i + dE_i$,

$f(E_i, E, x)dE$ — the probability for an incident proton with the energy E_i, to have in the target at a distance x, its energy in the interval E, $E + dE$,

$\sigma(E)$ — cross-section for the energy E.

Each element can be identified by one or several peaks whose surface N_R is related to $Y(E_p, t)$ by:

$$N_R = n_p \, \varepsilon \, Y(E_p, t) \qquad (2)$$

where ε — detector efficiency,

n_p — the number of incident protons.

The analytical form of the function $f(E_i, E, x)$ has been discussed elsewhere.[1] It is shown that the straggling is correctly evaluated by a Gaussian function whose variance is given by the Bohr relation.

In the case studied here, GaSb can be considered as an amorphous compound, and the variance will be:

$$\sigma^2 = 4\pi \, e^1 \, N \, (Z_{Ga} + Z_{Sb}) \, x \qquad (3)$$

where N — the number of molecules of Ga Sb per cm^3,

$Z_{Ga}(Z_{Sb})$ — the atomic number of Ga (or Sb).

The fluctuations in energy of the incident beam, represented by $g(E_p, E_i)$, are smaller than the straggling of the beam in the target. Thus, to a good approximation, $g(E_p, E_i)$ can be represented by the delta function $\delta(E_p, E_i)$.

The other parameters required are the cross-sections for the (p, p'γ) reactions. For ^{28}Si and ^{32}S we have measured the resonant and the non-resonant contributions (Figs 1 and 2). The numerical data in the case of ^{68}Zn, where resonances are not observed, are shown in Fig. 5a.
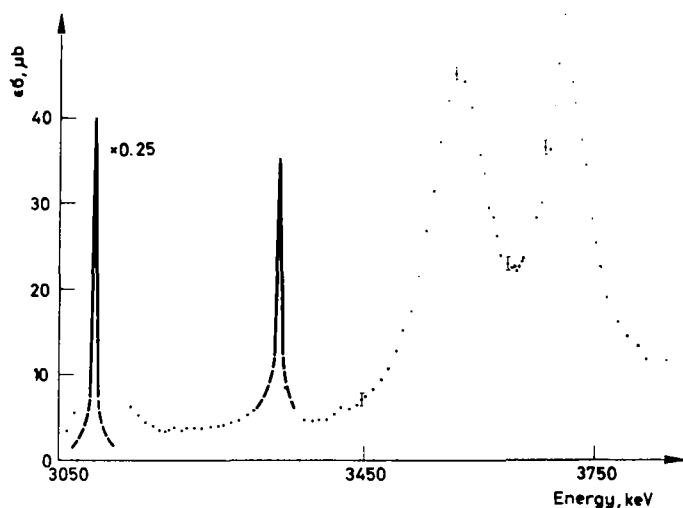
Fig. 1. Cross-section for the ^{28}Si(p, p'γ)^{28}Si reaction
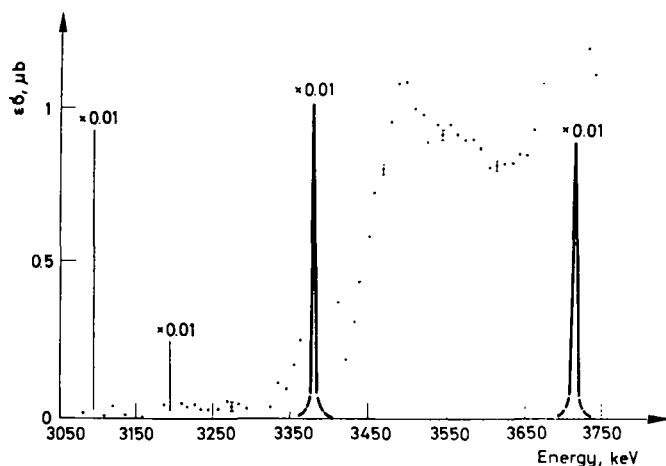
Fig. 2. Cross-section for the ^{32}S(p, p'γ)^{32}S reaction

Experimental results

The Van de Graaff accelerator of our Center, with maximum energy of 4 MeV, has been used to produce a 0.15 μA proton beam. This intensity is limited by the heat transfer to the target and by the counting rate of the electronic chain. The charge deposited on the target is deduced from the current by means of an ELCOR integrator. The thickness of the target is typically 0.1 mm.
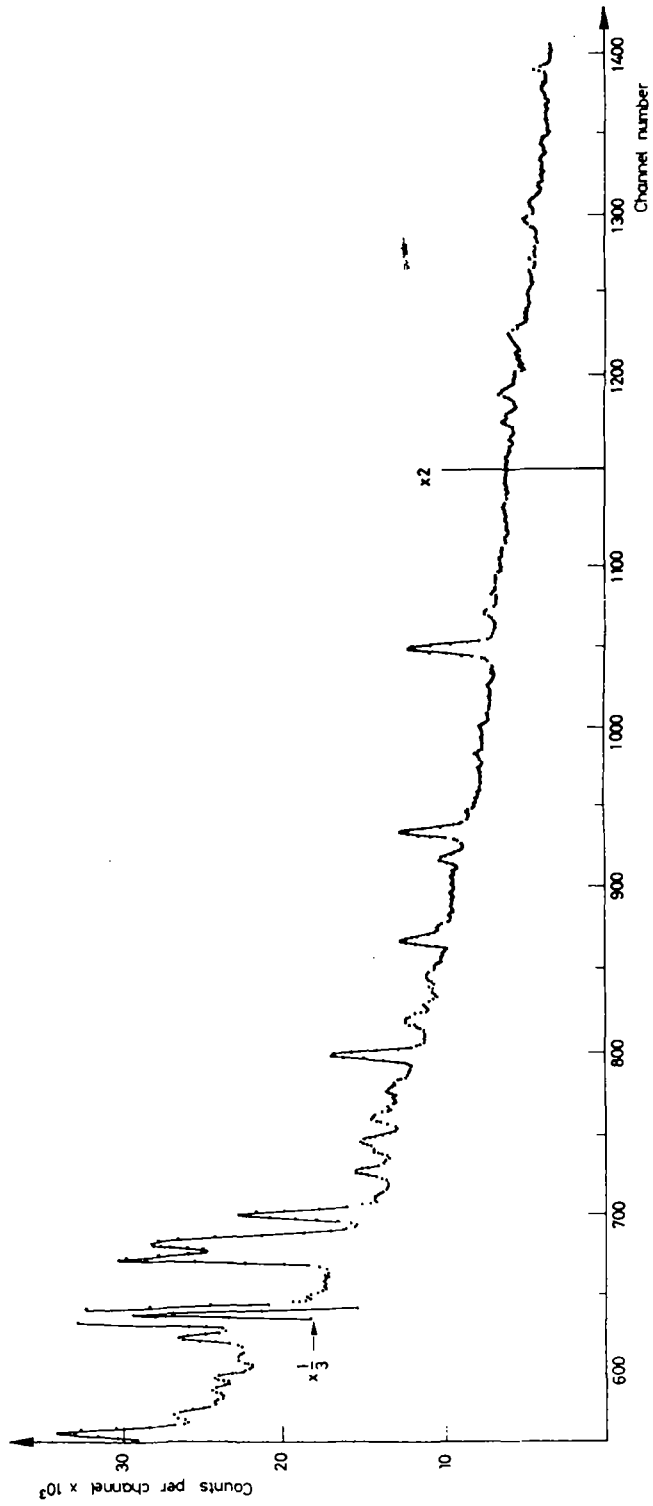
Fig. 3. γ-Spectrum resulting from the interaction of 3 430 keV protons with an ultrapure thin Ga target

The protons are detected in a 40 cm^3 Ge(Li) diode. Pulses are analysed in a conventional electronic system: TENNELEC TC 135 charge preamplifier, TENNELEC TC 200 amplifier and a 4096 multichannel analyser (INTER-TECHNIQUE).

Fig. 3 gives the example of the γ-spectrum resulting from the irradiation of a thin ultrapure Ga target evaporated onto a tantalum foil for $E_p = 3\ 430$ keV. Another spectrum corresponding to the GaSb target is shown in Fig. 4; the positions of photopeaks for $E_\gamma = 1\ 779$ keV (^{28}Si) and $E_\gamma = 2\ 230$ keV (^{32}S) are indicated. If the presence of the 1 779 keV γ-ray is evident, the situation is less clear for the 2 230 keV transition. A comparison of Figs 3 and 4 indicates that the high counting rate produced with Ga atoms will make important the data processing of the GaSb spectra. A programme including three operations: additions of GaSb spectra, smoothing and subtractions of Ga, has been written for an I.B.M. 360-44.

Analysis of Zn

This experiment allows a study of the sensitivity in detecting an impurity in a lattice matrix with similar Z and A values. The number of atoms will be deduced from the reaction yield and the surface of the photopeaks, by means of Eqs (1) and (2). In the case of Zn no resonances are found for the (p, p'γ) reactions. Thus we can determine only a mean number of atoms per cm^3.

The use of isotopes ^{64}Zn and ^{66}Zn is not possible due to the presence of peaks for the corresponding energies $E_\gamma = 992$ keV and $E_\gamma = 1\ 039$ keV in the Ga spectrum. The choice is restricted to the unfavorable isotope ^{68}Zn which presents a smaller cross-section and isotopic ratio; in this case the γ-ray energy is 1 078 keV.

Fig. 5b shows a part of the GaSb spectrum around $E_\gamma = 1\ 078$ keV obtained after the data processing ($E_p = 3\ 700$ keV).

We have attributed the low-intensity peak to the ^{68}Zn transition for the following reasons:

(a) the energy agrees rigorously with the energy of the first 2^+ level of ^{68}Zn;

(b) the shape of this peak is comparable with the low-intensity peaks observed in the γ-spectrum in the Ga target;

(c) the variation of its intensity with the charge after partial Ga subtraction is a linear function while, under the same conditions, the Ga peaks vary slowly (Fig. 6).

The mean number n of ^{68}Zn atoms is deduced from Eqs (1) and (2); we find $n = 1.1 \cdot 10^{19}$ at $\cdot$ cm^{-3}. The precision of this result depends mainly on the error in the evaluation of N_R and in the determination of $\sigma(E)$. In this case, the relative error is about 70%.

Analysis of Si and S

In our sample where doping was made with S, we found a high contamination of Si. These elements are detected simultaneously. The proton energy is $E_p = 3\ 430$ keV. In this case the resonance $E = 3\ 379$ keV in the ^{32}S(p, p'γ)^{32}S reaction takes
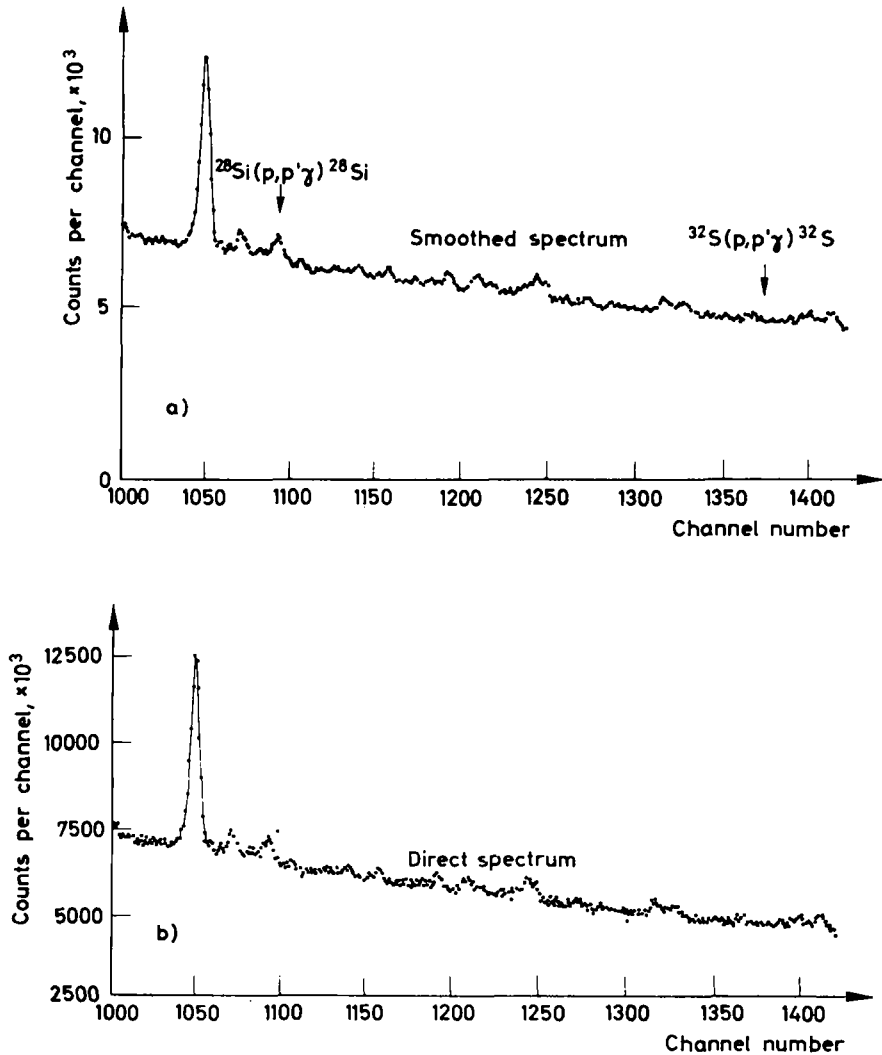
Fig. 4. Part of the γ-spectrum resulting from the interaction of 3 400 keV protons with a GaSb target. The expected positions of impurities (Si and S) are indicated

place at a distance $x = 2.4\ \mu$m from the front face of the target. The characteristics of the resonances observed for Si and S are given in Table 1.

Fig. 7 shows two parts of the GaSb spectra corresponding to the photon energies $E_\gamma = 1\ 779$ keV (^{28}Si) and $E_\gamma = 2\ 230$ keV (^{32}S). The photopeak for the ^{32}S transition corresponds to the Channel 1 371.

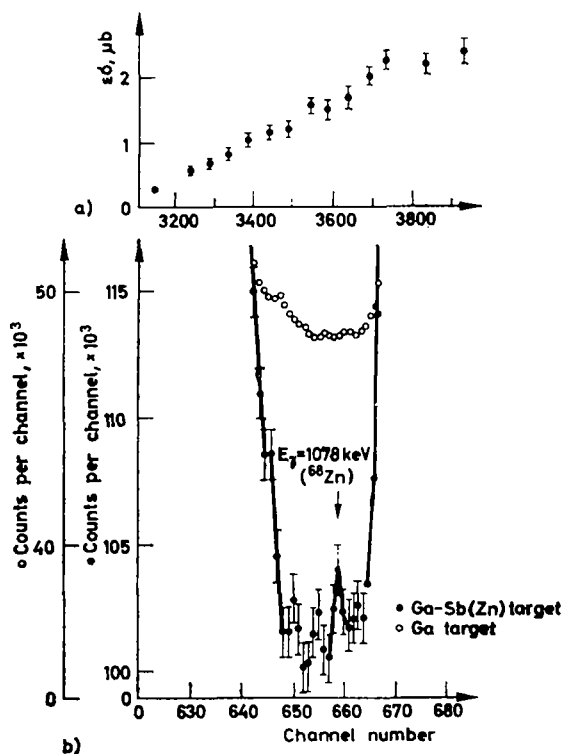Fig. 5. a — Cross-sections of the $^{68}Zn(p, p'\gamma)^{68}Zn$ reactions ($E_\gamma = 1\,078$ keV). b — Part of the γ-spectrum corresponding to the position of the 1 078 keV γ-ray

Table 1

Characteristics of the resonances used for the detection of Si and S. The resonant parts A_R^i are indicated by 1, 2, 3. A_{NR} is the non-resonant part of the reaction for an incident energy of protons of 3.4 MeV

i	E_R, keV	Γ, keV	$\varepsilon\sigma_R$, 10^{-30} cm²	$\dfrac{\pi}{2}\dfrac{\varepsilon\sigma_R\Gamma}{K}$, 10^{-33} cm³	A_R, 10^{-33} cm³	A_{NR}, 10^{-33} cm³
Microanalysis of Si						
1	3 100	8	157±16	9.0		
2	3 335	8.5	37± 4	2.3	11.3	5.6
Microanalysis of S						
1	3 094	0.34	91± 9	0.2		
2	3 195	0.44	25± 2	0.1	2.0	0.2
3	3 379	2.2	101± 9	1.7		

It is very similar to the ^{68}Zn peak and the same comments can apply to its characterization. The photopeak for the ^{28}S transitions is more apparent (Channel 1 093); in this case the subtraction of the Ga contribution is not needed and we expect a better precision in the result.
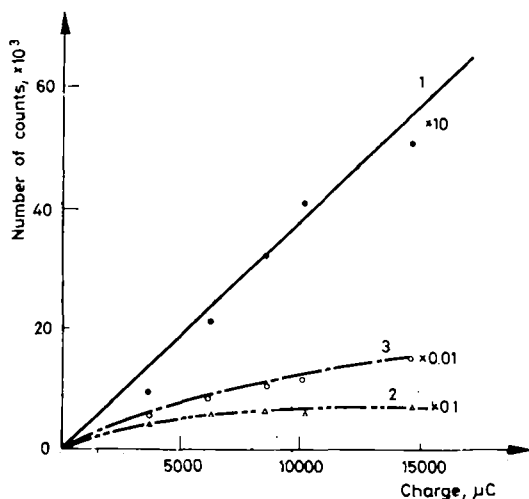

Fig. 6. Variations of intensity of the peaks with the charge for ^{68}Zn, ^{69}Ga and ^{71}Ga. The gallium contribution has been partially subtracted. 1 — ^{68}Zn(p, p'γ)^{68}Zn, 2 — ^{69}Ga(p, γ)^{70}Ge, 3 — ^{71}Ga(p, n)^{71}Ge

The number N_R of detected photons results from the resonant and the non-resonant cross-sections:

$$N_R = n_p n (A_R + A_{NR}).\qquad(4)$$

The contribution of the resonances whose sum is A_R, can be evaluated from Eq. (2):

$$Y_{(\infty,\infty)} = \frac{\pi}{2}\frac{1}{K}\varepsilon\,\sigma_R\Gamma.\qquad(5)$$

A_{NR} is calculated from Eq. (1) where a polynomial expression fitted to the experimental values has been used for $\sigma(E)$.

Finally, if three resonances appear (as for example in ^{32}S), we write:

$$N_R = n_p n\left[\frac{\pi}{2}\left\{\left(\frac{\varepsilon\,\sigma_R\Gamma}{K}\right)_1 + \left(\frac{\varepsilon\,\sigma_R\Gamma}{K}\right)_2 + \left(\frac{\varepsilon\,\sigma_R\Gamma}{K}\right)_3\right\} + \iint \varepsilon f(E_p, E, x)\,\sigma_n(E)\,dE\,dx\right].$$

The values of the different parameters are given in Table 1. It should be noted that in the case of ^{32}S the greatest part (about 80%) of N_R results from the 3 379 keV resonance. As already indicated, it takes place for $x = 2.4\ \mu$m; from the

values of the straggling and of the width of the resonance we estimate that the thickness of GaSb involved in this resonance is 0.2 μm. Thus, the number of sulphur atoms is not a mean number, but really the quantity of sulphur localized in that part of the target; we find $n = 2.4 \cdot 10^{19}$ at $\cdot$ cm^{-3}, with a relative precision $\Delta n/n = 35\%$.

For the analysis of the silicon atoms, two resonances are taken into account: 3 100 and 3 335 keV (Table 1). The non-resonant part is fairly important. The number of Si atoms is: $n = 3.5 \cdot 10^{19}$ at $\cdot$ cm^{-3}, with $\Delta n/n = 20\%$. The localization is less precise than in the case of sulphur atoms, due to the fact that the width of the resonance is much higher for ^{28}Si than for ^{32}S.

Conclusion

Comparison with (d, p) or (d, α) reactions

It is interesting to compare our results and the values expected from other reactions such as (d, p) or (d, α). In Table 2 are given the main characteristics of these reactions for impurities and lattice atoms: Q value, number of levels in the interval of excitation energy $0-2$ MeV, cross-section, deuteron energy. The (d, α) reactions whose Q values are lower for Si and S than for the Ga isotope are excluded. For (d, p) reactions, we observe that:

— the Q values are similar for ^{28}Si, ^{32}S and Ga isotopes. The separation of the proton groups will be a difficult problem;

— the (d, p) cross-sections have been measured for Si and S; for Ga they have been estimated from the ^{69}Zn(d, p)^{70}Zn reaction. In the best case the ratio of differential cross-sections is:

$$\frac{\left(\dfrac{d\sigma}{d\Omega}\right)_{Si, S}}{\left(\dfrac{d\sigma}{d\Omega}\right)_{Ga}} \simeq 10$$

— the number of levels excited in (d, p) reactions is much higher for Ga than for Si or S.

Sensitivity

Theoretically, the sensitivity of the method depends only on the influence of the lattice matrix. In the special cases studied here, the sensitivities ϕ for Zn, Si and S are 300 ppm, 90 ppm and 700 ppm, respectively. In a lattice whose atoms would be less reactive, we think that our method can give better results in sensitivity, in precision and in duration of the experiment.

Sensitivity ϕ can be expressed in other units. For example, in a surface analysis of sulphur atoms, we find $\phi = 2.4 \cdot 10^{14}$ at $\cdot$ cm^{-2}. The weight of sulphur taking

Table 2

Characteristics of (d, p) and (d, α) reactions for Si, S and Ga atoms

Reaction	Q, Mev	Numbers of levels in the first 2 MeV of the residual nucleus	$\dfrac{d\sigma}{d\Omega}$ mb/sr (average value)	E_d	Reference
^{28}Si(d, p)^{29}Si	6.253	3	0.7	2.5	4
^{32}S(d, p)^{33}S	6.418	8	0.1	2	5
^{69}Ga(d, p)^{70}Ga	5.41	14	0.1*	2.5	6
^{71}Ga(d, p)^{72}Ga	4.295	18			7
^{28}Si(d, α)^{26}Al	1 432	8	1	7	8
^{32}S(d, α)^{30}Si	4.892	5	0.4	2.5	
^{69}Ga(d, α)^{67}Zn	9.24				
^{71}Ga(d, α)^{69}Zn	9.00				

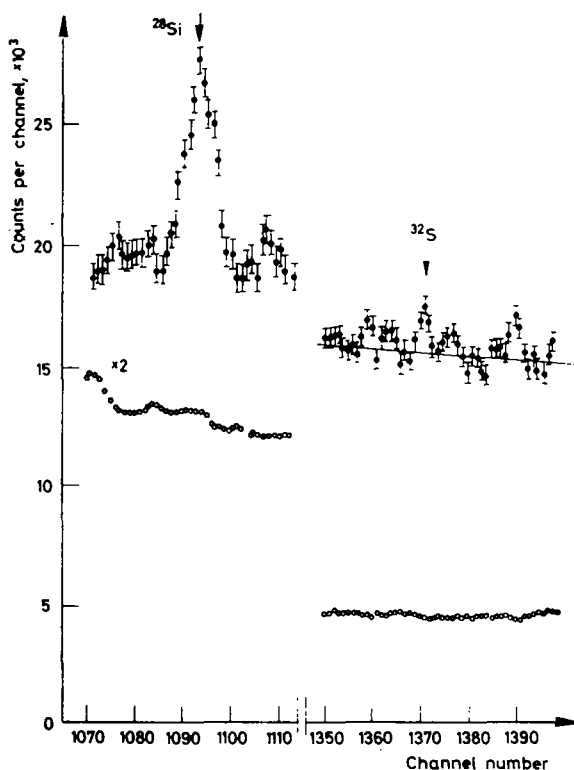* Evaluated by comparison with the ^{68}Zn(d, p)^{69}Zn reaction.

Fig. 7. Parts of the γ-spectrum (GaSb target) after additions, smoothing and subtraction of Ga. The peaks attributed to Si and S, and the corresponding parts of the Ga spectrum are indicated
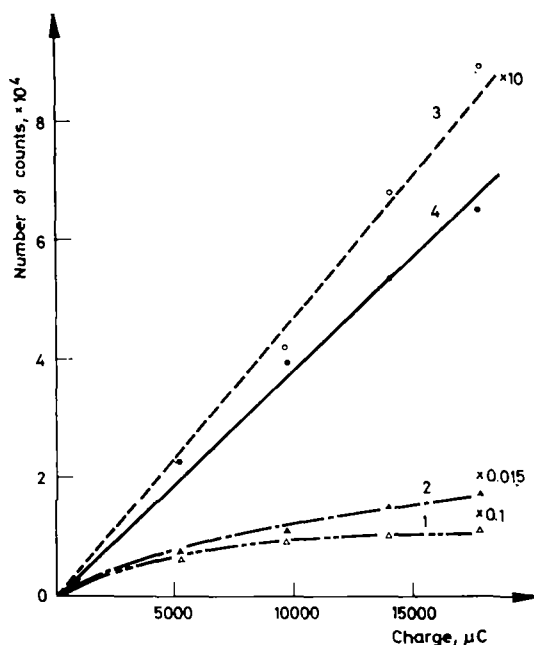
Fig. 8. Variations of intensity of the peaks with the charge for ^{28}Si, ^{32}S, ^{69}Ga and ^{71}Ga. The gallium contribution has been partially subtracted. $1 - {}^{71}Ga(p, n\gamma)^{71}Ge$, $2 - {}^{69}Ga(p, \gamma)^{70}Ge$, $3 - {}^{32}S(p, p'\gamma)^{32}S$, $4 - {}^{28}Si(p, p'\gamma)^{28}Si$

an active part in the detection is quite low: $\phi = 0.12 \cdot 10^{-9}$ g. This result is compared in Table 3 with other classical methods quoted by MORRISON.[2] Our method seems quite interesting for the elements studied; the sensitivity is similar to that for spark mass spectrometry, but it allows localization and gives the absolute number of atoms.

Table 3

Comparison between the absolute limits of sensitivity (in nanograms) for Si, S, Zn, quoted by MORRISON[2]

Method	Element		
	Si	S	Zn
Spectrophotometry	100	100	100
Fluorescence	80	200	1 000
Atomic absorption	6 000		0.3
Flame spectrophotometry	700	2 000	80
Neutron activation	5	500	10
Spark source mass spectroscopy	0.03	0.03	0.1

In conclusion, we think that the channelling phenomena of charged particles passing through crystalline structures can be used to improve the sensitivity, as indicated by DAVIES.[3] The interactions of the protons with the lattice matrix will be considerably reduced, while the reactions with interstitial impurities are not altered.

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