UM-P-78/68

APPLICATION OF THE RESONANT $^{52}Cr(p,\gamma)^{53}Mn$ REACTION TO THE MEASUREMENT OF CHROMIUM DEPTH DISTRIBUTIONS.

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ABSTRACT

A resonance in the $^{52}Cr(p,\gamma)^{53}Mn$ reaction has been investigated as a probe for the quantitative determination of chromium depth distributions. The relevant nuclear parameters of this resonance were measured to be: resonance energy, E_p = 1005.2 ± 0.2 keV, total width Γ < 100 eV, and resonance strength, $(2J+1)\Gamma_p\Gamma_\gamma/\Gamma$ = 0.89 ± 0.11 eV. As an example of the use of the nuclear resonance technique, the chromium profile of an electroplated chrome black solar absorber surface has been studied and the results are presented.

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1. Introduction

Surface coatings of chromium are used in a wide variety of applications, from the formation of electrical contacts in microcircuits to corrosion reduction in steels and the production of ornamental finishes. When required, the thickness of a chromium layer can usually be determined by conventional techniques such as mass difference, x-ray fluorescence, etc. However, in some cases it is of interest to obtain information on the variation with depth of the chromium concentration.

In particular there exists a need for knowledge of the surface chromium profile of the non-uniform Cr containing film used in the manufacture of chrome-black solar absorber surfaces[1]. The photothermal properties of these surfaces are believed to depend critically upon the detailed chemical composition gradients within the film[2]. To date no technique has produced a convincing profile of the Cr distribution of such surfaces.

This paper describes the use of a resonance in the nuclear reaction $^{52}Cr(p,\gamma)^{53}Mn$ at a proton energy of 1005 keV as a non-destructive probe of the Cr depth concentration profile and its application to the case of chrome-black absorber surfaces.

The basic principles of the method are reviewed briefly in the next section. In many instances of practical interest, this use of a nuclear resonance method seems preferable to use of the familiar elastic backscattering technique[3] as Cr-containing targets may be comprised of thick substrate materials having atomic masses close to Cr and usually slightly higher (e.g. steel, copper). The analysis of the resultant overlapping energy spectra of the backscattered particles is then extremely difficult.

2. Nuclear Resonance Technique

The use of resonant nuclear reactions to determine the concentration of certain elements as a function of depth in solid samples is now a familiar technique which has been extensively documented in the literature (see e.g. ref[4]). The applicability of the technique depends on the existence of an isolated strongly excited resonance in a nuclear reaction involving an isotope of the element to be analysed. Inspection of the energy level scheme shown in Fig. 1 suggests the suitability of a resonance in the $^{52}Cr(p,\gamma)^{53}Mn$ reaction at $E_p \sim 1005$ keV, where E_p is the proton bombarding energy. We note that this reaction involves the most abundant Cr isotope, ^{52}Cr, with a natural abundance of 83.8%. Gamma-ray yield curves have been measured in the vicinity of this resonance by a number of investigators[5,6]. Their results indicate that although there are five weak (p,γ) resonance within ± 100 keV of the 1005 keV resonance (at $E_p \approx 918$, 929, 953, 987 and 1025 keV), this resonance is about 10 times stronger than neighbouring resonances and so is well suited for quantitative depth profiling of surface Cr films.

Prior to the present study the total width of the (p,γ) resonance has not been well determined but appeared to be < 1 keV[5] which is sufficiently narrow for most profiling purposes.

The variation in Cr concentration of a Cr-containing layer may be determined by measurement of the (p,γ) yield as a function of proton beam energy. At any proton energy, E_o, greater than the resonance energy, E_r, the measured yield will be proportional to the Cr concentration at a depth x_o where

$$x_o = \frac{(E_o - E_r)}{(-dE/dx)}$$

For the small range of proton energies usually of interest, the stopping power $-dE/dx$ is essentially independent of energy. Since, in section 3, the resonance width is shown to be small, for all practical purposes the depth resolution will be determined by the energy spread of the accelerated proton beam and energy straggling in the target. For a more general and complete discussion of the resonance technique, see ref[7].

3. Experimental details and results

In order for this resonance technique to have maximum utility, it was felt necessary to measure precisely the resonance energy, total width and strength of the $^{52}Cr(p,\gamma)^{53}Mn$ resonance near 1005 keV. To this end a natural chromium target was prepared by evaporating spectroscopic grade Cr onto a 0.025 cm thick gold backing. The target thickness was determined by conventional mass difference methods and found to be 236 ± 16 $\mu g/cm^2$. An upper limit of 5% on the oxygen content of this target was inferred by comparison of the 871 keV γ-ray yield from the $^{16}O(d,p_1\gamma)^{17}O^*$ reaction from the Cr target and a reference Cr_2O_3 target at a deuteron energy of 2 MeV. The target was mounted in a stainless steel target chamber which was maintained at a pressure near 5×10^{-6} torr by an ion pump.

Proton beams were delivered by the University of Melbourne 5U Pelletron accelerator. Before impinging normally on the target, the defocussed beam was defined by an 8mm diameter aperture which was followed by an electron suppressor ring maintained at -500 V. The target chamber consituted a deep Faraday cup. Typical beam currents were 3 μA.

The γ-ray yield curve was measured by a 68 cm^3 Ge(Li) detector placed at 0^o with its front face 2 cm from the target. Since the (p,γ) resonance populates a spin - ½ compound nucleus state[8], the de-excitation γ-rays have an isotropic angular distribution. The semi-thick target yield curve was obtained by

measuring the photopeak yield of 378 keV γ-rays which corresponded to the first excited state to ground state transition in ^{53}Mn. According to the branching ratio data of Shulte et al[6], approximately 69% of all γ-cascades feed the first excited state. Use of the Ge(Li) detector in the present experiment circumvented any problems about resolving the γ-ray contributions from proton-induced reactions on the other Cr isotopes, particularly ^{53}Cr[5]. The detector photopeak efficiency for 378 keV γ-rays was measured with the aid of calibrated sources.

Figure 2 shows the data for one pass in fine energy steps over the 1005 keV resonance. Data taking was begun at a proton energy of 1000 keV and points were taken at intervals of 500 eV reducing to 125 eV on resonance. Gamma ray data were acquired for 300 micro Coulomb of integrated current and 4096 channel spectra were recorded at each point. Once the plateau was sufficienty well defined for the ^{52}Cr(p,γ) reaction, the target was moved out of the path of a beam and a sodium-containing target was positioned in the beam path. By monotonically increasing the proton beam energy, γ-ray yield curves were traced out for the ^{23}Na(p,p$_1$γ) reaction resonant at E_p = 1008.77 ± 0.10 keV[9] by observing the 440 keV γ-ray and for the ^{23}Na(p,α$_1$γ) reaction resonant at E_p = 1010.5 ± 0.3 keV[9] by observing the 1634 keV γ-ray. The ^{52}Cr(p,γ) resonance energy was then established against the reference ^{23}Na + p resonances with the aid of the known magnetic field calibration of the accelerator analysing magnet[10]. The value of this resonance energy was found to be 1005.2 ± 0.2 keV which is in agreement with an earlier value of 1005.8 ± 1.0 keV[8] but is more precise.

In order to assign an upper limit to the resonance width, Γ, the leading edge of the semi-thick target yield curve was compared with the usual theoretical function $[\frac{1}{2} + \frac{1}{\pi} \tan^{-1}\{(E-E_r)/(\frac{1}{2}\Gamma)\}]$ where E_r is the resonance energy.

In figure 2 this function is shown by the dashed curve for Γ = 0.075 keV. This approach provides only an approximate upper limit to the resonance width because once widths of the order of 100 eV are to be investigated, a careful analysis of the leading edge shape is required. At this level of precision, effects such as the Lewis effect[11] (for which there is some evidence in the yield curve of Fig. 2), and Doppler broadening due to the thermal motion of the target atoms[12] must be carefully folded into the line shape. For example, one may estimate the Doppler width, Δ, in the classical approximation, $\Delta = (4\ mEkT/M)^{\frac{1}{2}}$ where m,M are the projectile and target masses, respectively, E is the bombarding energy and T the equilibrium target temperature. Then Δ = 50 eV for ^{52}Cr + p at 400°K. This value is not too different from the observed interquartile distance of the yield curve. Additionally a beam energy spread of ~ 100 eV has been found to be characteristic of proton beams from the Pelletron for the beam geometry typical of this experiment. Consquently although the leading edge line shape has not been unambiguously analysed it seems reasonable to place an upper limit of 100 eV on the (p,γ) resonance width.

A complete (p,γ) excitation function for the 1005 keV resonance is shown in Fig. 3 by the open circles. The measured energy width of this yield curve is 33 ± 1 keV. This is consistent with the value of 32 keV from a calculation of energy loss based upon the measured mass density and the tabulated stopping power[13] for 1 MeV protons of 11.8 eV per 10^{15} atoms of Cr. In order to calculate the resonance strength, we start with the standard definition of (p,γ) resonance strength, in the thin target approximation which is [14,15]

$$\left.\frac{(2J_r+1)\Gamma_p\Gamma_\gamma}{\Gamma}\right|_{lab.} = \left(\frac{A}{A+1}\right)^2 \frac{M_p\, E_r\ (2J_p+1)(2J_t+1)}{(\pi\lambda\!\!\!^{-})^2\, t}\ Y$$

where J_p, J_t and J_r are the spins of the proton, target nucleus (in this case ^{52}Cr) and the resonance level, respectively; A is the mass number of the target, M_p is the proton mass, E_r is the laboratory resonance energy and t the areal

density of the (^{52}Cr) target. Then Y is the total number of γ-rays emitted per incident proton as the beam energy is swept so that every nucleus in the target has the opportunity to be excited. This yield is obtained from the experiment by integrating data such as those shown in Fig. 3. Corrections were applied for Ge(Li) detector 378 keV γ-ray photopeak efficiency, branching through the 378 keV level, summing effects due to the coincident detection of more than one γ-ray of the cascade and isotope abundance of the natural Cr target.

The value obtained for the resonance strength was 0.89 ± 0.11 eV. The alternative analysis of the semi-thick target yield data in terms of the step in the yield curve[14,15] using tabulated stopping powers provided a value for the resonance strength completely consistent with the above result. This agreement is to be expected given the good correspondence between the observed energy width of the yield curve and the value predicted from the known mass of the target as discussed earlier.

A value for this resonance strength of 2.0 ± 0.6 eV has been reported by Maripuu[8] in significant disagreement with the present result. The resonance strength literature is characterized by discrepancies of this magnitude for many reactions. Recently Paine et al[16] demonstrated experimentally that uncertainties in the assumed target composition may be frequently responsible for errors in resonance strength determination. As Maripuu[8] provides few details of his experiment, especially the properties of the target, we are unable to suggest an explanation for this discrepancy.

4. Application to chrome black

The quest for more efficient solar absorbers has resulted in the development of numerous coating techniques for the absorption panel itself. Efficient flat-plate solar collectors should have high absorptivity in the visible spectrum and low infrared emissivity. One such class of solar absorbers is fabricated by

coating a metal of high infrared reflectivity with a thin film that is transparent in the infrared but highly absorbing in the visible, where solar radiation is concentrated. Amongst the most widely used thin film systems are the selective black absorbers[1] of which electrodeposited black chrome coatings are a prime example[2].

A sample was obtained of a chrome black surface. A detailed description of the sample preparation technique as well as a summary of its photothermal properties is given in ref[2]. Briefly the chrome black surface was prepared by a 70 second electroplating from a Cr-containing bath[17] onto a polished nickel-plated copper substrate. This sample was mounted in the target chamber at the end of the Pelletron beam line and a (p,γ) excitation function traced out. At a proton energy of 1005 keV, γ-ray contributions from reactions on Ni and Cu in the target were found to be insignificant. The measured yield curve is shown in Fig. 3 by the filled points.

Such an excitation function in association with a yield curve for a metallic Cr target of known thickness, then provides the following information:

i) The Cr content of the chrome black surface was found to be 59 ± 5 $\mu g/cm^2$ by comparing the areas under the yield curves in Fig. 3,

ii) Assuming that oxygen is the only other constituent (as is expected to be the case[2]), then the average composition of the chrome-black is $Cr\ O_{0.4}$. This follows from the ratio of the plateau heights which vary inversely with the respective stopping powers. Such an average composition may arise, for example, if the chrome black film is made up of grains which are Cr-rich and are contained within Cr_2O_3 shells.

iii) As the high energy tail of the yield curve appears greater than that due only to straggling the film thickness is either non-uniform or there is a decrease in Cr concentration with depth. A careful fitting of the yield curve (as described, for example, in ref[15])

would be required for more quantitative information.

iv) Assuming that the stopping power of this chrome black sample to be that of a Cr $O_{0.4}$ compound, then the proton energy scale may be converted to depth if the target volume density is known. This density is uncertain but may be assumed to lie between that of Cr (7.2 g/cm^3) and Cr_2O_3 (5.2 g/cm^3). Adopting a value of 6.7 g/cm^3 then provides a conversion factor of 10 keV = 1000 Å. The chrome black film thickness then becomes approximately 1500 Å.

5. Summary

The resonance at E_p = 1005.2 keV in the $^{52}Cr(p,\gamma)^{53}Mn$ reaction appears well suited to the quantitative determination of Cr concentrations and depth profiles. The (p,γ) resonance technique is especially appropriate to those cases where samples contain elements with atomic numbers greater than that of Cr as, with their higher Coulomb barrier, the associated γ-ray contribution is usually much less. The relatively low value of this resonance energy also leads to the following attractive features:

i) the absence of a high γ-yield from most (p,p'γ) reactions and

ii) the absence of neutrons to damage the Ge(Li) detector (the nearest (p,n) threshold likely to be of concern is at E_p = 1406 keV for the reaction $^{53}Cr(p,n)^{53}Mn$).

In addition, as most van der Graaff installations can provide a 1 MeV proton beam the technique is readily applicable.

Acknowledgements

We would like to acknowledge valuable discussions with Dr. S. Solomon regarding the application of resonance techniques to Cr profiling. We thank Dr. B. Window for making available the chrome black sample. The assistance of B. Szymanski and P. Menon throughout the running of the Pelletron accelerator was greatly appreciated.

References

1) D.M. Mattox, J. Vac. Sci. Tech. 13 (1976) 127; 12 (1975) 1023.

2) B. Window, I.T. Ritchie and K. Cathro, Appl. Optics (1978) in press.

3) W.K. Chu, J.W. Mayer, M. Nicolet, T.M. Buck, G. Amsel and F. Eisen, Thin Solid Films 17 (1973) 1.

4) J.R. Bird, B.L. Campbell and P.B. Price, Atomic Energy Review (IAEA) 12 no. 2 (1974) 275.

5) S.E. Arnell, Arkiv. Für Fysik 21 (1961) 177.

6) R.L. Schulte, J.D. King and H.W. Taylor, Nucl. Phys. A243 (1975) 202.

7) Z.E. Switkowski, J.C. Overley, S-C. Wu, C.A. Barnes and J. Roth, J. Nucl. Mat. (1978) in press.

8) S. Maripuu, Nucl. Phys. A149 (1970) 593.

9) P.M. Endt and C. van der Leun, Nucl. Phys. A214 (1973) 1.

10) J.C.P. Heggie and Z.E. Switkowski, Nucl. Instr. and Meth. 147 (1977) 425.

11) H.W. Lewis, Phys. Rev. 125 (1962) 937.

12) J.M. Donhowe, J.A. Ferry, W.G. Mourad and R.G. Herb, Nucl. Phys. A102 (1967) 383.

13) Hydrogen stopping powers and ranges in all elements, eds. J.F. Ziegler and H.H. Andersen (Pergamon, N.Y.) 1977.

14) H.E. Gove, Nuclear Reactions Vol. 1 (1959), eds. P.M. Endt and M. Demeur (North-Holland, Amsterdam) p259.

15) Z.E. Switkowski, R. O'Brien, A.K. Smith and D.G. Sargood, Aust. J. Phys. 28 (1975) 155.

16) B.M. Paine, S.R. Kennett and D.G. Sargood, Phys. Rev. C17 (1978) 1550.

17) L. Sivaswamy, S. Gouri and B.A. Shenoi, Metal Finishing 72 (1974) 48.

Figure Captions

Figure 1. Partial energy level scheme for the $^{52}Cr(p,\gamma)^{53}Mn$ reaction. The separation energies for the respective two particle system, $^{52}Cr+p$, $^{49}V+\alpha$ and $^{52}Mn+n$ are given by the numbers on the ground state bars. The approximate position and relative strength of the (p,γ) resonances near the 1005 keV resonance are shown. (Data were taken from refs.[5,6]).

Figure 2. Yield curve of the $^{52}Cr(p,\gamma)^{53}Mn$ reaction at the E_p = 1005 keV resonance. Error bars represent statistical uncertainties only. For these magnetic field settings, the relationship 1G = 1 keV holds approximately. The significance of the dashed curve is discussed in the text. The small off-resonance yield arises from contributions from lower energy resonances. It is evident that these resonances should not significantly complicate Cr profile analyses based upon the 1005 keV resonance.

Figure 3. Variation of 378 keV γ-ray photopeak yield as a function of incident proton energy. The open circles refer to the standard metallic chromium target. The filled circles refer to the chrome black surface. Error bars are statistical uncertainties only. The dashed line shows the calculated plateau height for a target with the composition of the most stable chromium oxide, Cr_2O_3.

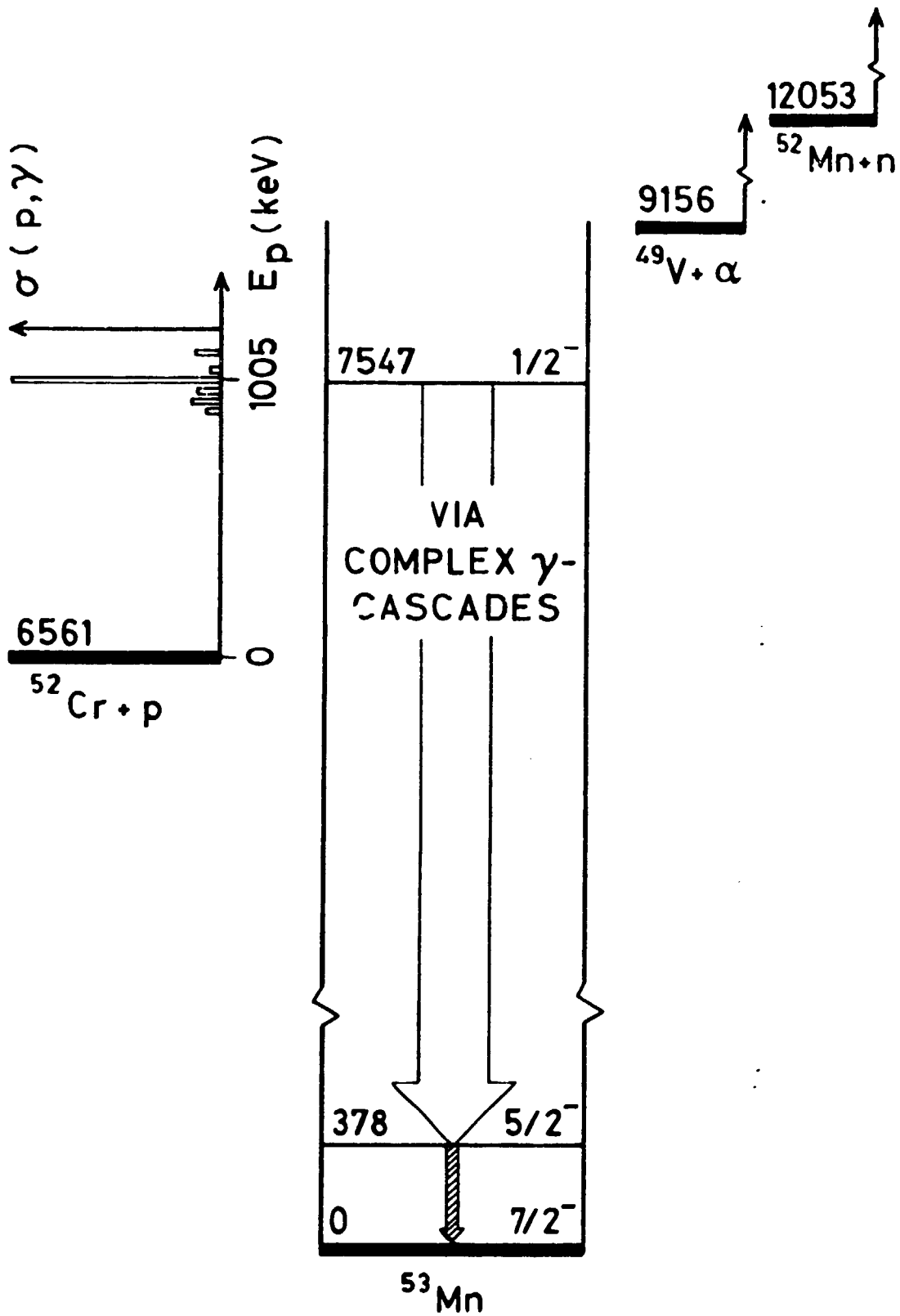

12053
52Mn+n
9156
49V+α
σ(p,γ)
Ep(keV)
1005
7547
1/2⁻
VIA
COMPLEX γ-
CASCADES
6561
0
52Cr+p
378
5/2⁻
0
7/2⁻
53Mn

Fig 1.

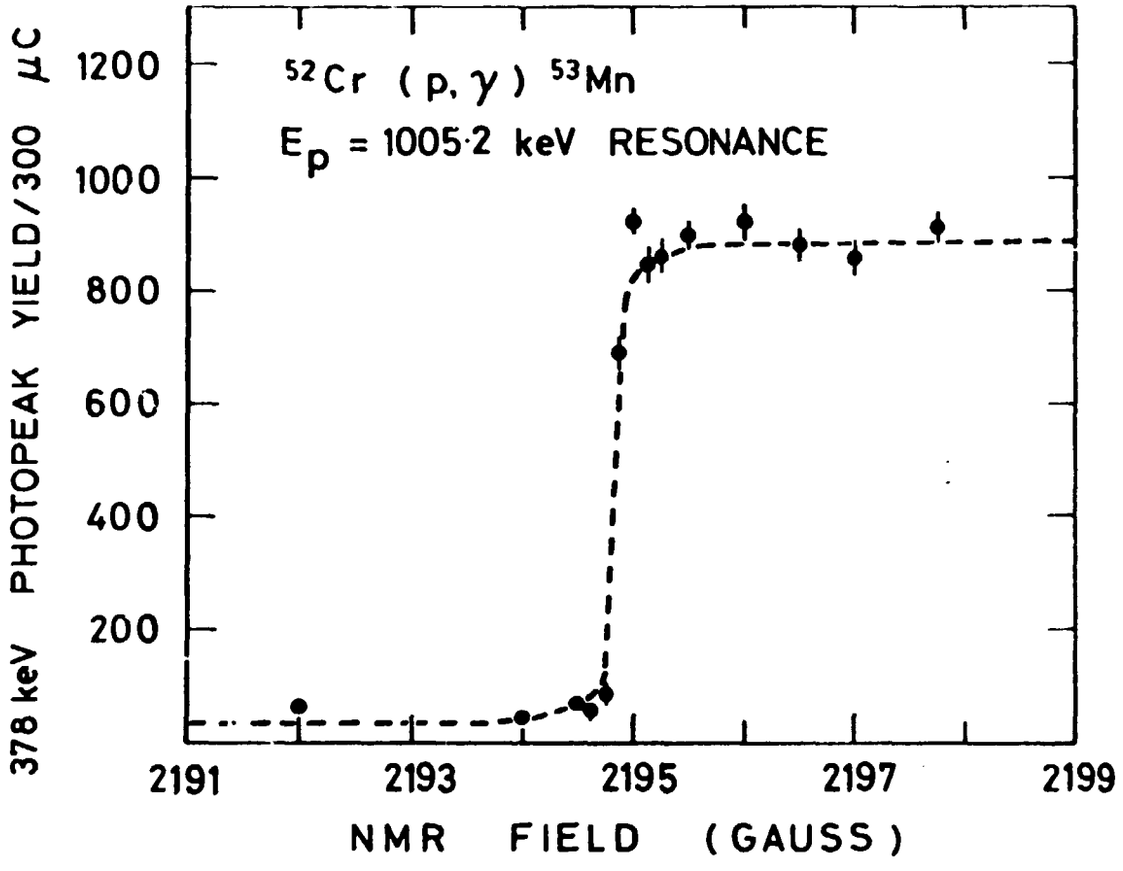
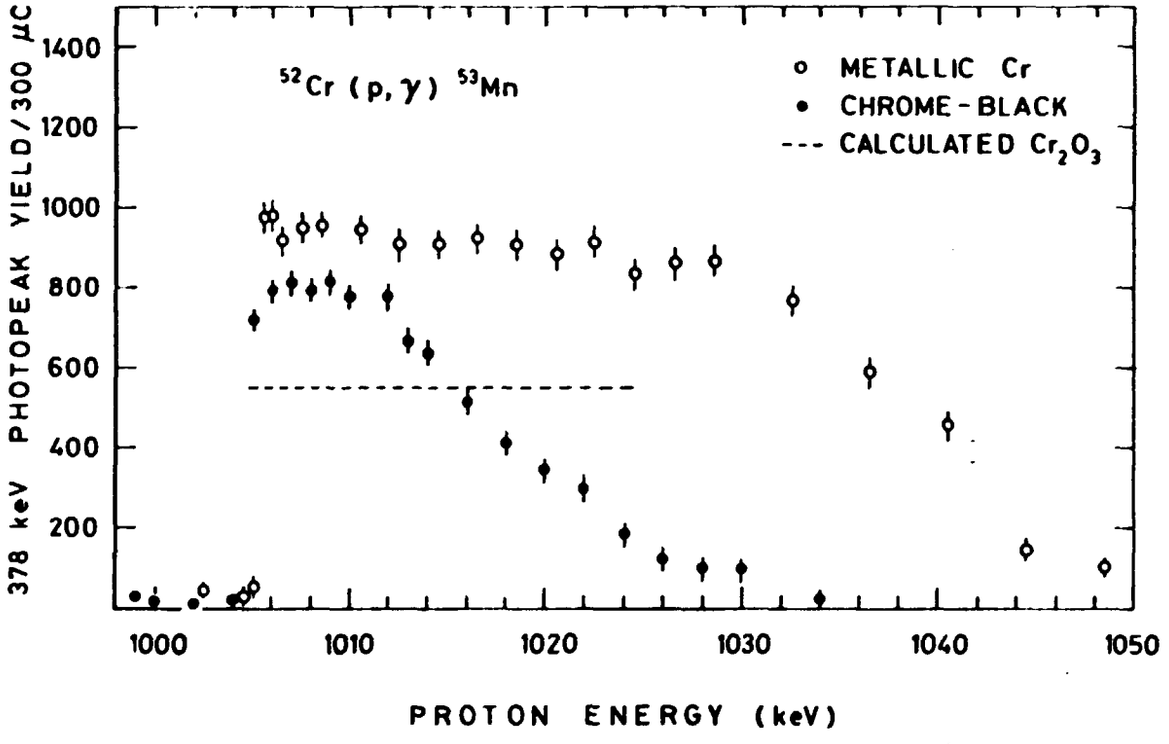

^{52}Cr (p, γ) ^{53}Mn
E_p = 1005·2 keV RESONANCE
378 keV PHOTOPEAK YIELD / 300 μC
1200
1000
800
600
400
200
2191
2193
2195
2197
2199
NMR FIELD (GAUSS)

Fig 2


$^{52}Cr\ (p,\gamma)\ ^{53}Mn$
METALLIC Cr
CHROME-BLACK
CALCULATED Cr_2O_3
378 keV PHOTOPEAK YIELD/300 μC
1400
1200
1000
800
600
400
200
1000
1010
1020
1030
1040
1050
PROTON ENERGY (keV)