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THE EFFECT OF THE CHEMICAL STATE ON THE LIFETIME OF THE 24-SECOND ISOMER OF Nb^{90} *

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The rate of decay of a radioactive nucleus is generally unaffected by its chemical and physical environment. However, in 1947 Daudel[1] and Segrè[2] predicted that under certain conditions a dependence of the decay constant on the chemical and physical environment of the nucleus should be observable, and subsequently such a dependence was found experimentally in the K-capture decay of Be^7[3] and in the internal conversion decay of Tc^{99m}.[4,5,6] In this letter we report on an experiment by which a large change in the decay constant of the 24-second Nb^{90} isomer was observed following a change in the chemical state.

Recently Cooper et al.[7] proposed a partial decay scheme for Mo^{90} (Fig. 1) in which a very low energy isomeric transition in Nb^{90} was postulated. The transition was not detected directly, but an upper limit of 3 keV was placed on its energy. It is thus of interest to obtain evidence of the existence of this isomeric transition.

Such evidence might be obtained, if the transition energy is sufficiently low, by changing the chemical environment of the nucleus and thus altering its decay constant. (As pointed out by Daudel[1], the change in isomeric decay constant arises from a change in electron density near the nucleus.) In the case of the 2-keV isomeric transition in Tc^{99m}, Bainbridge, Goldhaber and Wilson[4] observed a difference of 0.3% in the decay rate of Tc^{99m} in the compounds $KTcO_4$ and Tc_2S_7. In the case of the Nb^{90} isomer, the chemical

bonding electrons are in the N and O shells of Nb, with binding energies $\lesssim 50$ eV. If the decay energy should be less than 200 eV (binding energy of the M_V shell), internal conversion could take place only in the N and O shells and appreciable chemical effects might be expected.

In the case of a short-lived daughter activity in equilibrium with a long-lived parent, a sudden change in decay constant of the daughter caused by a chemical reaction will perturb the equilibrium, which will again be restored with the half-period of the daughter in its altered environment. (By "chemical reaction" is meant a change in chemical state of the daughter, not a chemical separation of daughter from parent.) Such a chemical effect on the lifetime of Nb^{90m_1} has been demonstrated by an experiment in which an intensity change of the 122-keV E2 gamma ray (in cascade with the low-energy isomeric transition) was observed following a rapid chemical reaction. About 200 Nb foils (0.02 in^2 × 0.0005 in) were bombarded with 50 MeV protons, producing Mo^{90} by a p,4n reaction. Each foil, which contained Nb^{90m_1} in equilibrium with the Mo^{90}, was rapidly dissolved (1-2 sec) in a mixture of hot concentrated HNO_3 and HF, thus changing the chemical environment of the metastable state from metallic to that of a fluoride complex.

Immediately after the chemical reaction, a growth in activity was noted. A four-point growth curve was obtained by recording four successive gamma-ray spectra from a Ge(Li) detector for 18 seconds in each of the four 100-channel blocks of a 400-channel pulse-height analyzer. This procedure was repeated about 200 times to insure the statistical reliability of the data. The entire experiment was repeated at a later date and a lower counting rate was used so as to improve the resolution. The resulting gamma-ray spectra from the first block of 100 channels are shown in Fig. 2.

The resolved growth curve of the 122-keV photopeak was obtained by assuming that the background under the photopeak is constant (as it is on both sides of the photopeak) and subtracting this background value from the total number of counts under the photopeak (Fig. 3). A least-squares analysis of the four gamma-ray spectra was made in order to obtain an average value of the background.

The expression for the intensity of the 122-keV gamma ray after the reaction is obtained from the usual relationship for the growth and decay of a two component system,

$$N_{Nb^{90m_1}} = \frac{\lambda_{Mo^{90}} N^{\circ}_{Mo^{90}}}{[(\lambda_{Nb^{90m_1}} + \Delta\lambda) - \lambda_{Mo^{90}}]} \{\exp(-\lambda_{Mo^{90}} t) - \exp[-(\lambda_{Nb^{90m_1}} + \Delta\lambda)t]\} + N^{\circ}_{Nb^{90m_1}} \exp[-(\lambda_{Nb^{90m_1}} + \Delta\lambda)t] , \quad (1)$$

where $N^{\circ}_{Mo^{90}}$ and $N^{\circ}_{Nb^{90m_1}}$ are the number of nuclei present at the time of the chemical reaction and $\lambda_{Nb^{90m_1}} + \Delta\lambda$ is the decay constant for the isomer in the fluoride complex. By substituting $\lambda_{Nb^{90m_1}} N^{\circ}_{Nb^{90m_1}}$ for $\lambda_{Mo^{90}} N^{\circ}_{Mo^{90}}$ in Eq. (1) (equilibrium condition immediately before the reaction) and dropping $\lambda_{Mo^{90}}$ from the denominator one obtains

$$N_{Nb^{90m_1}} (\lambda_{Nb^{90m_1}} + \Delta\lambda) = \lambda_{Nb^{90m_1}} N^{\circ}_{Nb^{90m_1}} \exp[-\lambda_{Mo^{90}} t] + \Delta\lambda N^{\circ}_{Nb^{90m_1}} \exp[-(\lambda_{Nb^{90m_1}} + \Delta\lambda)t] . \quad (2)$$

Thus the intensity of the 122-keV gamma ray is given by either the sum or difference (depending on the sign of $\Delta\lambda$) of 2 exponentials,

$$I(t) = \alpha \exp[-\lambda_{Mo^{90}} t] + \beta \exp[-(\lambda_{Nb^{90m_1}} + \Delta\lambda)t] \quad . \qquad (3)$$

Thus, $\beta/\alpha = \Delta\lambda/\lambda_{Nb^{90m_1}}$, the fractional change in decay constant of the isomer.

The functional relationship of Eq. (3) was fitted to the four points of the growth curve by the method of least squares. The best solutions (Fig. 3) were obtained with a Nb^{90m_1} half life of 21 sec, which is in good agreement with the 24 ± 3 sec value reported by Mathur and Hyde.[8] The results of this analysis show that the decay constant of the metal is 3.6 ± 0.4% greater than the decay rate of the fluoride complex.

The size of the effect, an order of magnitude greater than that observed by Bainbridge et al.[4] with Tc^{99m} in Tc metal and $KTcO_4$, indicates that the transition depopulating the 24-sec isomeric state has a very low energy and decays by internal conversion in the outermost electron shells, where changes in the chemical state can be expected to affect most strongly the electron density at the nucleus. So far as we know, this 3.6% change is the largest alteration in half-life yet noted for a radioactive isotope.

Not only is the effect an order of magnitude greater but it is also in the opposite direction from the effect observed in Tc^{99m}. Slater[9] suggested that the faster decay rate observed for $KTcO_4$ is due to a greater squeezing of the Tc atom in the $KTcO_4$ (Tc-O bond distance of 1.7 Å) as compared with the metal (Tc-Tc bond distance of 2.7 Å).[9] The same effect of smaller bond distance should also be present in the case of the solid Nb

fluoride salt, $KNbF_7$, since it has a Nb-F bond distance of 2.0 Å[10] compared with the Nb-Nb metal bond distance of 2.85 Å.[11] We have no knowledge of the Nb-F bond distance in the niobium fluoride complexes in the solution which was the final state in our experiment, but if it is also less than the Nb-Nb bond distance in the metal, another explanation must be sought for the direction of the observed effect. Possibly this could be attributed to the very high electronegativity of the fluorine atom. Since the Nb-F chemical bond involves essentially the 4d and 5s electrons, our results would then indicate that an appreciable fraction of the isomeric decay takes place by ejection of valence electrons, which would indeed indicate a very low energy transition.

We wish to thank Dr. G. Struble for the use of his least-squares spectrum analysis program and Dr. D. A. Shirley for helpful discussions and suggestions. Thanks are also due the crew of the 88" cyclotron for their help in carrying out the bombardments.

FOOTNOTES AND REFERENCES

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FIGURE CAPTIONS

Fig. 1. Partial decay scheme of Mo^{90} as proposed by Cooper et al.[5] The first metastable state (Nb^{90m_1}) at 122.5 + δ keV is indicated by m_1 and the second metastable state (Nb^{90m_2}) at 380.0 + δ keV is m_2.

Fig. 2. Accumulated gamma-ray spectra from the first 18 second counting interval after the chemical reaction, showing the 122-keV photopeak of Mo^{90} decay and the 133- and 142-keV photopeaks of Nb^{90} decay. Spectra A and B were taken at different counting rates.

Fig. 3. a) Growth curve of the 122-keV photopeak (A) intensity and plot of the background at lower and higher energies. The solid line indicates the least-squares fit to the points.

b) Growth curve of the 122-keV photopeak (B) intensity and plot of the background at lower and higher energies. The solid line indicates the least-squares fit to the points.

Fig. 4. Comparison of the experimental growth curves obtained from spectrum A and spectrum B. The B results were normalized to the first point of the A results by multiplying all B points by 2.865.

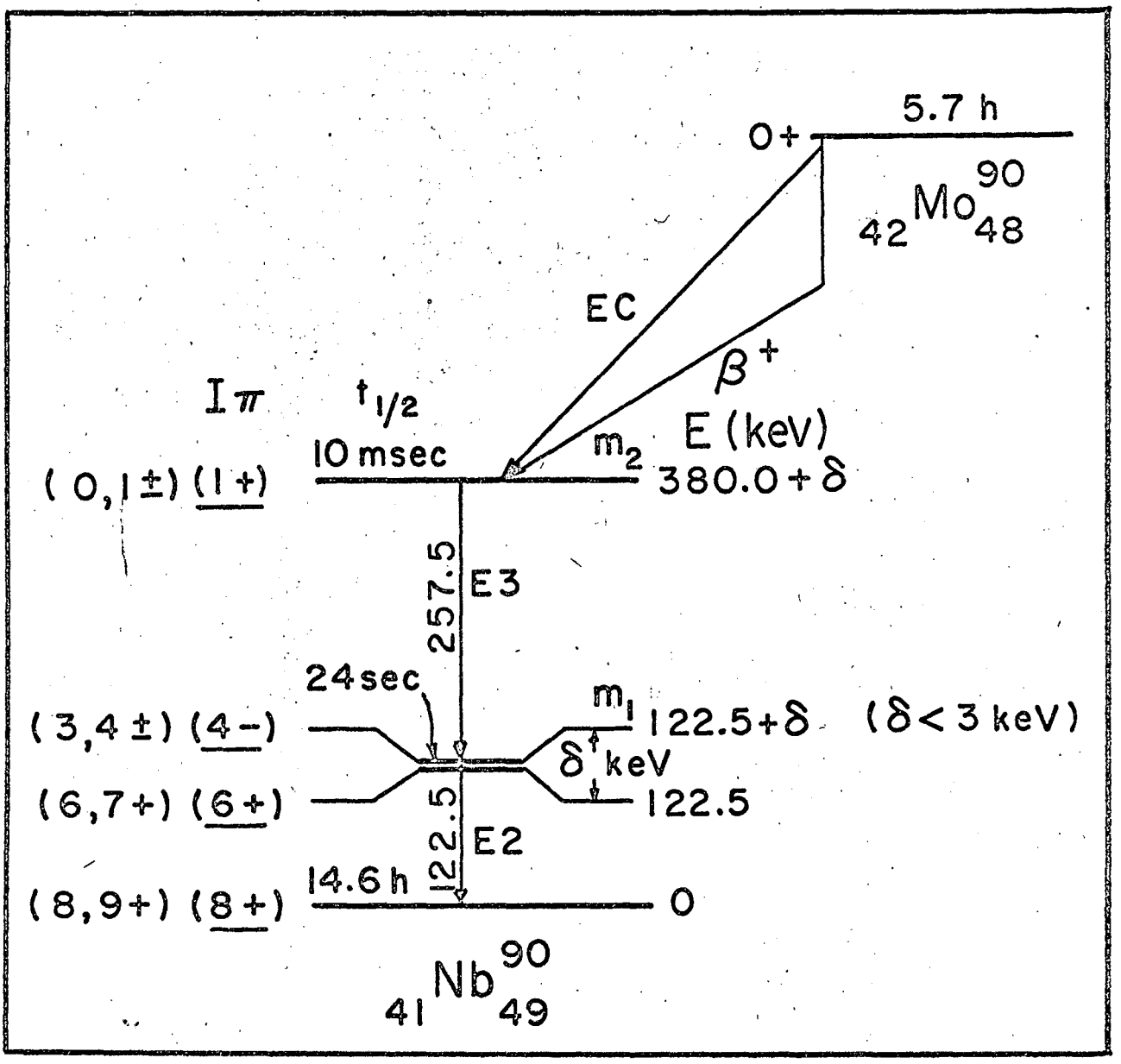

Fig. 1

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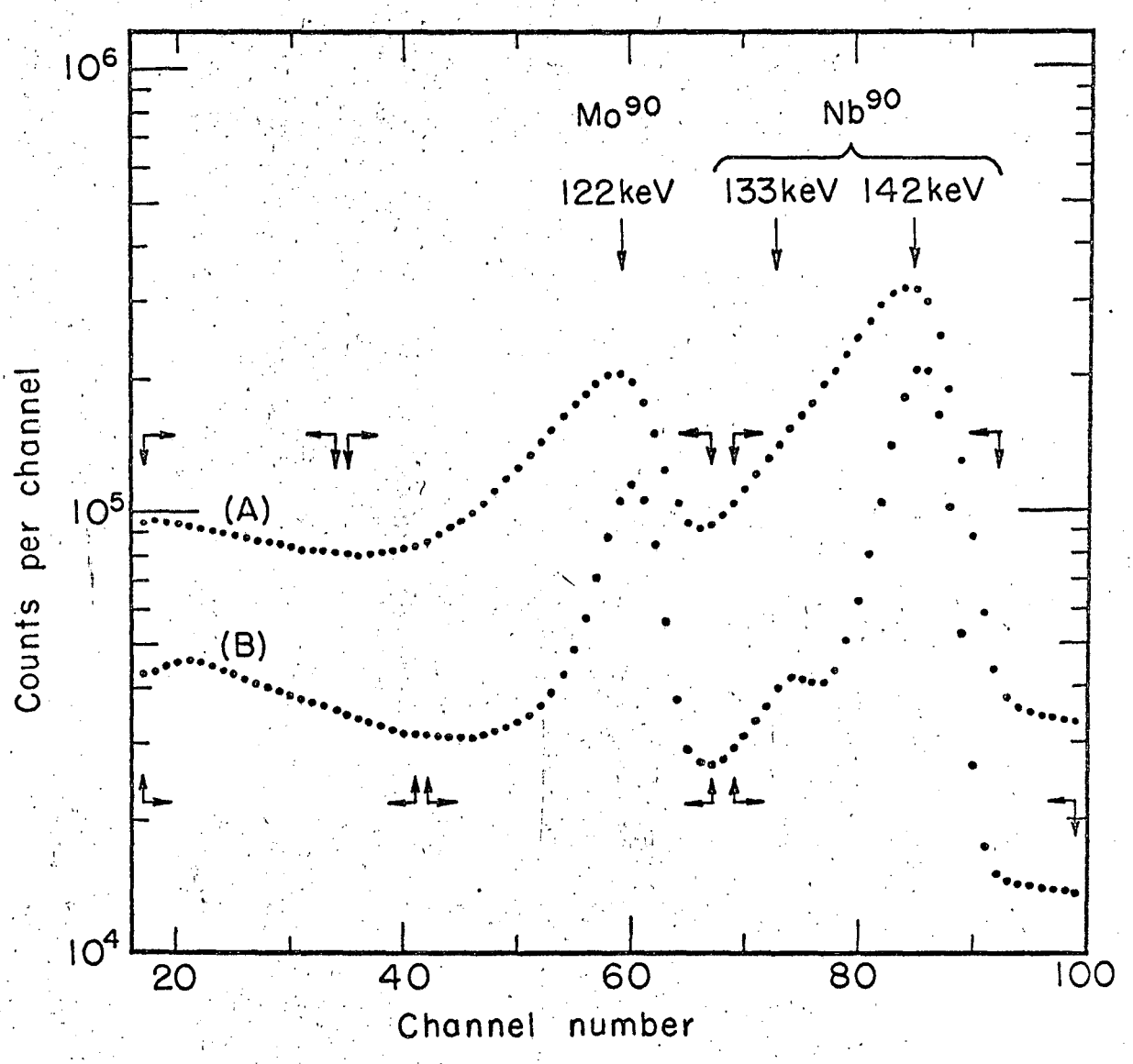
10^6
10^5
10^4
Counts per channel
Mo^{90}
Nb^{90}
122keV
133keV
142keV
(A)
(B)
20
40
60
80
100
Channel number

MUB-7290

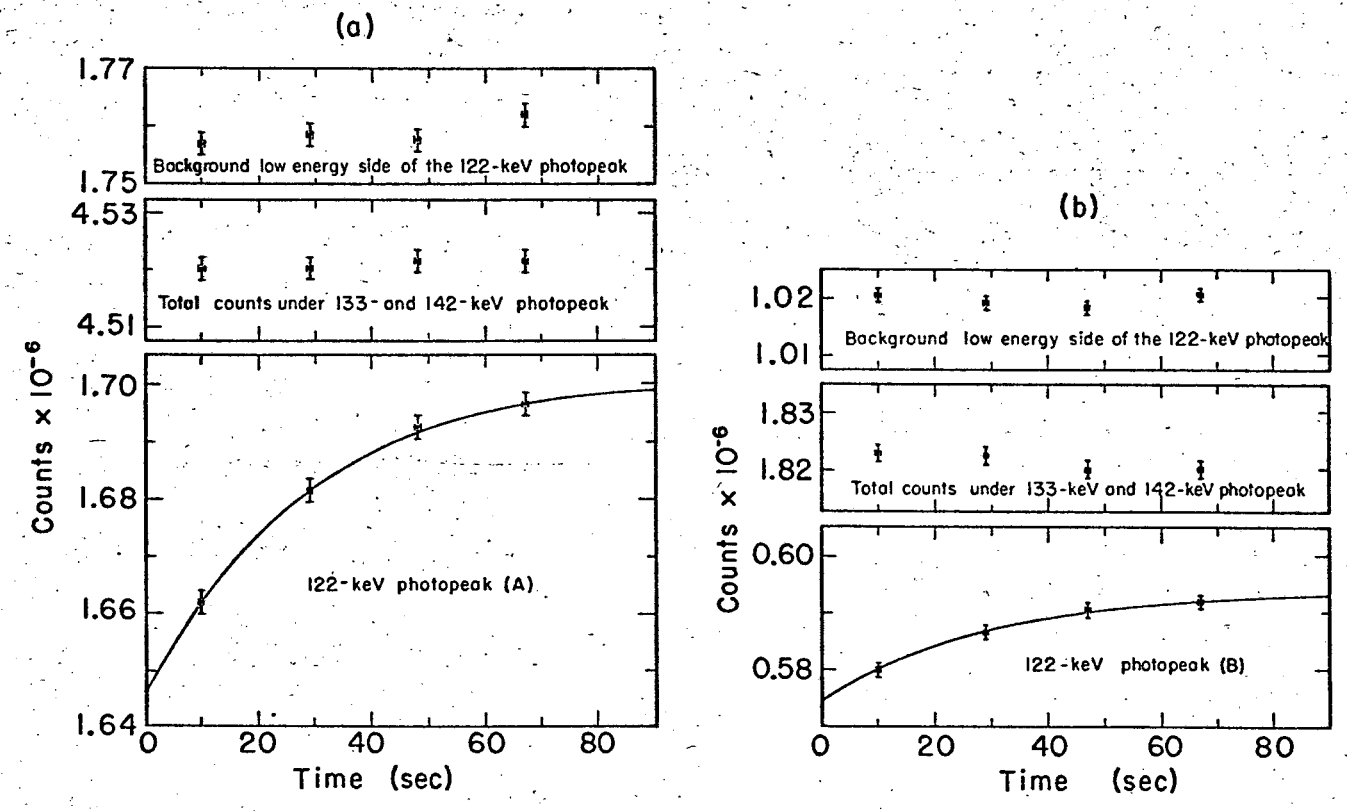

Fig. 3

MUB-7291

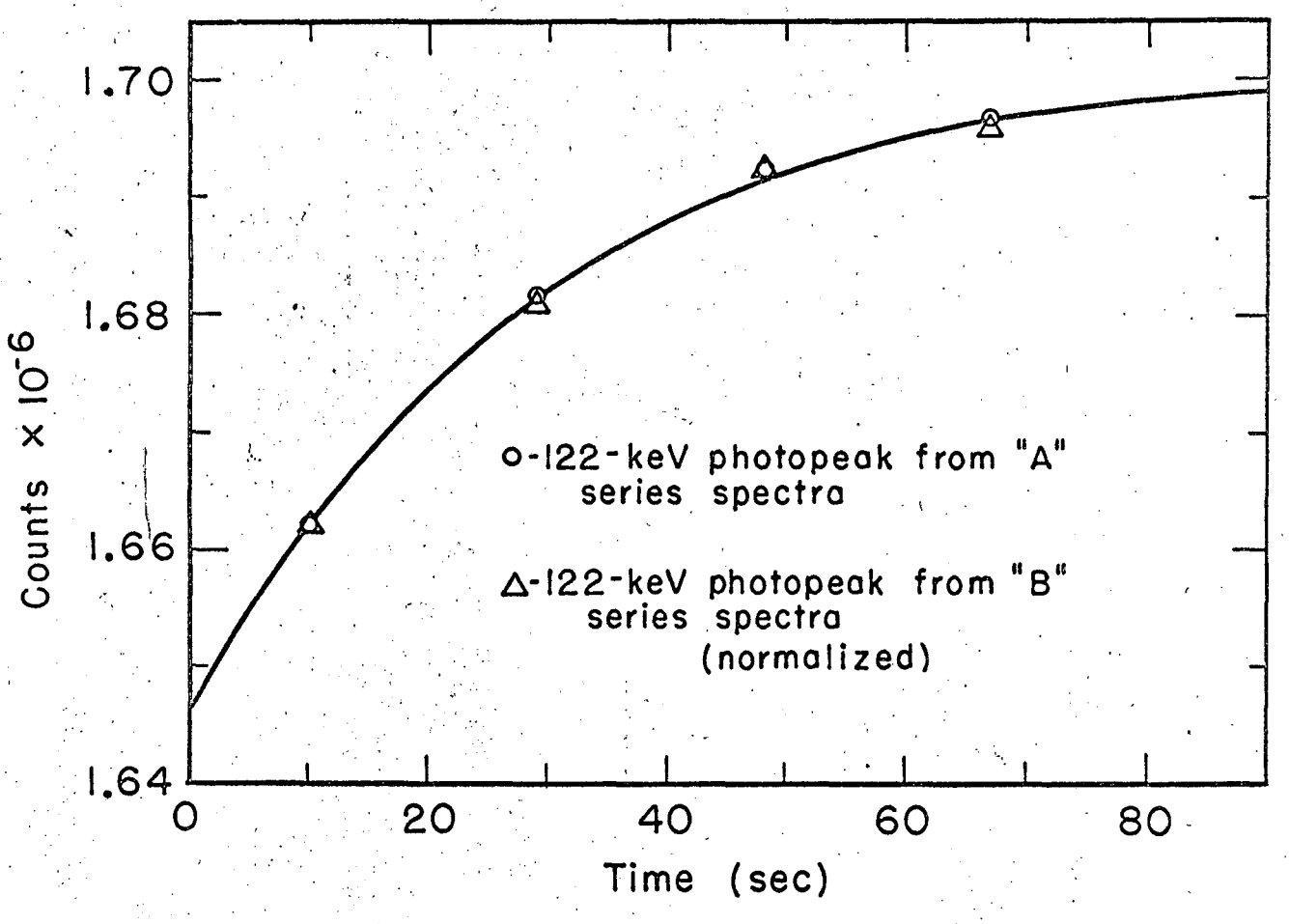

Fig. 4

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