

tals, are lower than these values. This agrees with experience, since sc TlCl and TlBr are the normally stable phases. The second consequence is a lowering of the longitudinal-phonon frequency, which together with the increase of  $\omega_T$  (due to increasing bond strength) is necessary to fulfill the Lyddane-Sachs-Teller relation: For fcc thallous halides the ratio  $\epsilon_0/\epsilon_\infty$  lies between 2 and 3, whereas for sc thallous halides this ratio is almost 7<sup>9</sup>; thus the ratio  $\omega_L/\omega_T$  should range between 1.4 and 1.8 (fcc) instead of being close to 2.6 (sc). A detailed calculation of the phonon frequencies of fcc thallous halides has to be waited for; an experimental determination is lacking too. From the arguments and experiments known up to now, however, it seems justified to ascribe to the fcc thallous halides a noticeably higher degree of covalency than to the sc ones.

In conclusion, I feel, that a straightforward application of the PV theory to ten-electron systems, whereas it may yield reasonable results for the electronic dielectric constant, is doubtful as far as ionicities are concerned. It is hoped that this work on the thallous halides will be a stimulus for examination or re-examination of other ten-electron systems, such as lead chalcogenides, or similar systems, e.g., lead and bismuth halides.

The author is indebted to W. Staude, H. Overhof, and K. Heidrich of many helpful discussions.

<sup>1</sup>E.g., J. C. Phillips, Phys. Rev. Lett 20, 550 (1968),

and Rev. Mod. Phys. 42, 317 (1970), and *Covalent Bonding in Crystals, Molecules, and Polymers* (Univ. of Chicago Press, Chicago, Ill., 1969); J. A. van Vechten, Phys. Rev. 182, 891 (1969), and 187, 1007 (1969).

<sup>2</sup>See, e.g., B. F. Levine, Phys. Rev. B 7, 2591, 2600 (1973). A large amount of literature in this field is quoted here.

<sup>3</sup>B. F. Levine, J. Chem. Phys. 59, 1463 (1973); D. Schiferl, Phys. Rev. B 10, 3316 (1974).

<sup>4</sup>K. Heidrich, W. Staude, J. Treusch, and H. Overhof, Phys. Rev. Lett. 33, 1220 (1974), and to be published.

<sup>5</sup>The work of S. H. Wemple and M. Di Domenico, Phys. Rev. B 3, 1338 (1971), will not be helpful for the same reason, since it explains the behavior of the *electronic* dielectric constant alone. It should be noticed, however, that, if the dispersion energy  $E_d$  does not change between the fcc and sc phases, then the value of  $\beta$ , as defined by Wemple and Di Domenico, would take on the "covalent" value 0.35 in the fcc case as compared to the "ionic" value 0.27 for the sc case, as a consequence of lowering the coordination number.

<sup>6</sup>An extended description of this LCAO model will be given by J. Treusch, to be published.

<sup>7</sup>H. Overhof and J. Treusch, Solid State Commun. 9, 53 (1971); R. Z. Bachrach and F. C. Brown, Phys. Rev. 81, 818 (1970).

<sup>8</sup>D. A. Liberman, D. T. Cromer, and J. T. Waber, Comput. Phys. Commun. 2, 107 (1971).

<sup>9</sup>R. P. Lowndes and D. H. Martin, Proc. Roy. Soc., Ser. A 308, 473 (1969).

<sup>10</sup>For sc thallous halides Levine's calculated average gaps (Ref. 3) are in good agreement with this paper's values, the maximum deviation being smaller than 0.6 eV. This is not surprising, since they are derived from experimental values of  $\epsilon_\infty$ .

<sup>11</sup>E.g., C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1966), 3rd ed., pp. 89-98.

## Optically Induced Localized Paramagnetic States in Chalcogenide Glasses

S. G. Bishop, U. Strom, and P. C. Taylor  
*Naval Research Laboratory, Washington, D. C. 20375*  
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Optically induced ESR and absorption due to localized paramagnetic states in the forbidden gap have been observed in several semiconducting chalcogenide glasses below ~15 K. Analysis of the ESR spectra indicates that these centers are holes localized on chalcogens and are not directly associated with impurities.

It has long been argued that there exist in the forbidden energy gaps of amorphous semiconductors localized electronic states which might be attributable to dangling bonds, impurities, or other defects in the structure of the disordered solid.<sup>1</sup> Various studies of the optical<sup>2</sup> and elec-

tronic<sup>3</sup> properties of chalcogenide glasses have been interpreted in terms of such localized gap states, and densities of localized states in the range  $10^{17}$  to  $10^{19}$  cm<sup>-3</sup> eV<sup>-1</sup> have been inferred from the experimental results. The most contradictory experimental result concerning the exis-

tence of these gap states has been the failure to observe by electron-spin resonance (ESR)<sup>4</sup> or magnetic-susceptibility techniques<sup>5</sup> any evidence of paramagnetism in chalcogenide glasses which is not due to the presence of paramagnetic impurities. It can be argued that most of the localized states are doubly occupied and therefore not paramagnetic, and that the density of any unpaired electrons near the Fermi level is simply too small to be observable.<sup>3,4</sup> In this case, however, optical injection of electron-hole pairs should disturb the equilibrium distribution of electrons and produce a detectable density of unpaired spins. At least one unsuccessful attempt to detect an optically excited ESR in chalcogenide glasses has been reported previously.<sup>4</sup>

This Letter reports the first observation of optically induced, localized paramagnetic states in the forbidden energy gap of chalcogenide glasses. We have observed that irradiation of chalcogenide glasses at 6–15 K by light which efficiently excites photoluminescence<sup>6,7</sup> (light for which the absorption coefficient  $\alpha \cong 100 \text{ cm}^{-1}$ ) produces an electron-spin resonance which is not present before illumination, i.e., in the cold dark. Accompanying this induced ESR is the appearance of an induced optical absorption in the normally transparent spectral range from the band edge to near mid-gap. Both of these effects persist after cessation of illumination. In addition, subsequent prolonged irradiation of the sample with infrared light in the mid-gap induced-absorption band reduces the strength of or “bleaches” both the optically induced ESR signal and the induced absorption. Previous failures to observe the ESR in chalcogenide glasses<sup>4</sup> are apparently explicable by the fact that only a specific band of photon energies can successfully induce the paramagnetic states.

Samples of  $\text{As}_2\text{Se}_3$ ,  $\text{As}_2\text{Se}_{1.5}\text{Te}_{1.5}$ ,  $\text{As}_2\text{S}_3$ , and Se were prepared from 99.999% pure elemental constituents. Samples of  $\text{As}_2\text{S}_3$  which contained 500 ppm Sb and a few parts per million of iron impurities<sup>2</sup> were obtained from Servo Corporation. Most samples exhibited some form of ESR response in the cold dark due to the presence of paramagnetic impurities, but the samples singled out for detailed study exhibited no sharply defined spectral features in the ESR derivative spectrum near  $g=2$  ( $1.5 \leq g \leq 3.0$ ). In addition, one higher-purity sample of glassy  $\text{As}_2\text{Se}_3$  exhibited no cold dark ESR signal under the operating conditions employed in the observation of the optically induced ESR signal.

ESR spectra were obtained between 12 and 15 K with a standard 9.25-GHz bridge spectrometer and an optical access cavity. The ESR spectrometer output was first recorded in the cold dark, and then the samples were irradiated *in situ* with photon energies known to produce both efficient photoluminescence<sup>6,7</sup> and the induced absorption bands discussed below. In each case monochromatic light for which  $\alpha \cong 100 \text{ cm}^{-1}$  was used (2.4 eV in  $\text{As}_2\text{S}_3$ , 1.98 eV in Se, 1.78 eV in  $\text{As}_2\text{Se}_3$ , and 1.18 eV in  $\text{As}_2\text{Se}_{1.5}\text{Te}_{1.5}$ ). This  $\alpha$  corresponds to bulk absorption in the Urbach tails, characteristic of the absorption edges in chalcogenide glasses.<sup>1,2</sup> Irradiation of the cold samples in the cavity for 1 min with approximately  $1 \text{ mW/cm}^2$  of the prescribed interband wavelength induced a clearly observable ESR signal near  $g=2$  which was not present in the cold dark. The growth of the ESR intensity saturated after 10 or 15 min for this illumination intensity.

The optically induced ESR spectra (derivative of the absorption) observed in three of the glass compositions are shown in Fig. 1 along with the typical cold dark base line obtained in  $\text{As}_2\text{Se}_3$ . Although the signal-to-noise ratios of the three traces in Fig. 1 are poor by the usual ESR standards, the observed line shapes are sufficiently accurate and reproducible for us to extract estimates of the principal components of the  $g$  tensor. The three principal components of the  $g$  tensor for each glass, which are calculated from the observed derivative spectra using standard techniques for polycrystalline or glassy samples,<sup>8</sup> are 2.00, 2.13, and 2.21 in  $\text{As}_2\text{Se}_3$ , 2.00, 2.04, and 2.06 in  $\text{As}_2\text{S}_3$ , and 2.00, 2.09, and 2.16 in Se, where the error in each case is  $\pm 0.02$ . The optical activity of the ESR centers is further demon-

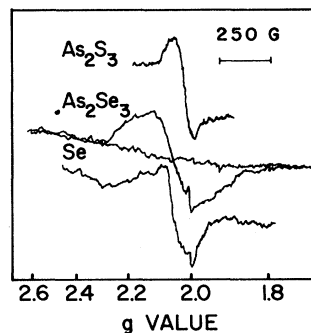


FIG. 1. Derivative of the optically induced ESR absorption at 9.243 GHz in glassy  $\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{Se}_3$ , and Se as a function of  $g$  value (arbitrary gain for each trace). All signals correspond to  $<10^{15}$  spins per sample.

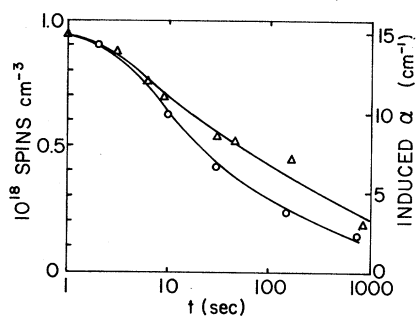


FIG. 2. Bleaching of saturated ESR (circles and left-hand scale) and optical absorption (triangles and right-hand scale) in glassy  $\text{As}_2\text{Se}_3$  for increasing time of exposure to  $\sim 3 \text{ mW/cm}^2$  of 1.24-eV light.

strated by the bleaching curve shown in Fig. 2. Here the intensity of the optically induced ESR spectrum in  $\text{As}_2\text{Se}_3$  is plotted as a function of increasing time of exposure to  $\sim 3 \text{ mW/cm}^2$  of 1.24 eV light. Similar bleaching curves were observed for appropriate energies in all of the glasses studied.

Optical-absorption experiments were carried out on the same samples employed in the ESR measurements. Hot-pressed or polished platelets of glass 100 to 500  $\mu\text{m}$  thick were cooled to 6 K on an optical cold-finger Dewar. The transmission of each sample was measured using low-level light intensity ( $\sim 10^{-2} \text{ mW cm}^{-2}$ ) and phase-sensitive detection techniques from the band edge down to about 0.4 eV, in which range the glasses are rather transparent. The sample was then irradiated with the prescribed band-gap light ( $\alpha \cong 100 \text{ cm}^{-1}$ ) whose intensity ( $\sim 1 \text{ mW cm}^{-2}$ ) was greater by two orders of magnitude than that with which the transmission was measured. After several minutes of irradiation, the sample transmission was again measured from the band edge to 0.4 eV with low-level light intensities. These experiments were most successful in  $\text{As}_2\text{Se}_3$  and  $\text{As}_2\text{Se}_{1.5}\text{Te}_{1.5}$  in which 5-min interband irradiations produced 10 to 15% reductions in the transmission below the band edge. These reductions correspond to induced absorption coefficients of  $\alpha > 10 \text{ cm}^{-1}$  in the 100  $\mu\text{m}$  penetration depth of the exciting light. The induced-absorption spectrum<sup>9</sup> for glassy  $\text{As}_2\text{Se}_3$  is shown in Fig. 3 along with the cold dark band-edge absorption curve. In  $\text{As}_2\text{S}_3$  glass, irradiation with  $500 \text{ mW cm}^{-2}$  of 5145- $\text{\AA}$  light from an argon ion laser was required to induce comparable absorption coefficients in the spectral range below the band edge while no optically induced absorption was observed in Se

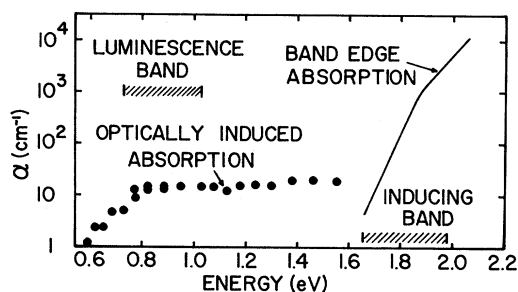


FIG. 3. Energy dependence of optically induced absorption in glassy  $\text{As}_2\text{Se}_3$  at 6 K.

in this spectral range using  $1\text{-mW}\cdot\text{cm}^{-2}$  inducing light intensity. (Although it was not possible to observe an induced absorption in glassy Se, an induced ESR signal was observable because of the greater sensitivity of the ESR measurement.)

The induced absorption is stable for several hours at 6 K. However, it can be bleached by the same procedure which bleaches the ESR spectrum, i.e., irradiation of the sample with photon energies corresponding to the induced absorption band with an intensity roughly equivalent to that of the interband exciting radiation. In Fig. 2 the induced absorption coefficient measured in glassy  $\text{As}_2\text{Se}_3$  (after a 5-min exposure to 1.78-eV light) is shown as a function of increasing exposure to  $3 \text{ mW cm}^{-2}$  of 1.24-eV light, which lies in the middle of the induced absorption band shown in Fig. 3. This near-infrared light gradually reduces the induced absorption *throughout* the induced absorption band. (Note that the number of induced ESR centers and the induced absorption coefficient exhibit roughly equivalent bleaching rates in Fig. 2 for roughly equivalent doses of bleaching radiation.) This bleaching of the induced absorption was observed for several bleaching wavelengths within the induced absorption bands of glassy  $\text{As}_2\text{Se}_3$ ,  $\text{As}_2\text{Se}_{1.5}\text{Te}_{1.5}$ , and  $\text{As}_2\text{S}_3$ .

The interband photon energies required to induce and the mid-gap energies required to bleach are the same for both the induced absorption and the ESR, and the growth and bleaching rates of the two effects are comparable. For this reason we attribute the induced optical absorption and paramagnetism to the same centers. Furthermore, estimates of the total density at saturation of the optically induced centers from the two independent measurements are in reasonable agreement. If one assumes that the upper limit for the optical cross section of an induced center is equivalent to that of an isolated defect such as

an  $F$  center<sup>10</sup> (with unity oscillator strength), then an estimated lower limit for the total density of states  $N \cong 10^{16} \text{ cm}^{-3}$  is obtained from the induced absorption coefficient in  $\text{As}_2\text{Se}_3$ . A second estimate of  $N$  can be obtained by comparing the integrated intensity of the optically induced ESR (assuming spin  $\frac{1}{2}$  for the center) with that of a calibrated standard sample. This procedure yields an upper bound of  $N = 10^{18} \text{ cm}^{-3}$  for  $\text{As}_2\text{Se}_3$ , although the actual value could be as much as a factor of 10 smaller due to experimental uncertainties. Hence the optical and ESR estimates place the total density of states in the range  $10^{16} \leq N \leq 10^{18} \text{ cm}^{-3}$  for  $\text{As}_2\text{Se}_3$ . The estimates of  $N$  based on the maximum ESR intensities induced by the  $\sim 1\text{-mW-cm}^{-2}$  light in the other glasses are  $10^{18} \text{ cm}^{-3}$  in  $\text{As}_2\text{Se}_{1.5}\text{Te}_{1.5}$ , and  $10^{17} \text{ cm}^{-3}$  in  $\text{As}_2\text{S}_3$  and Se.

Analysis of the ESR spectra in the various glasses strongly indicates that the optically induced centers are holes localized on chalcogens. First of all, the measured  $g$  values are all greater than the free-electron value indicating that if the centers are strongly localized, then they are holes. Secondly, the observed linewidths of the resonances in  $\text{As}_2\text{Se}_3$  and  $\text{As}_2\text{S}_3$  ( $\sim 250$  and  $\sim 75$  G, respectively) are too small to be consistent with a hole localized on an As atom. The Fermi contact contribution to the atomic coupling constant for As ( $\sim 4000$  G)<sup>11</sup> indicates that  $< 1\%$  of the unpaired spin density is in an arsenic  $s$  orbital. Also, the  $p$ -orbital atomic coupling constant for As ( $\geq 100$  G)<sup>11</sup> predicts a minimum linewidth for a spin predominantly localized in an arsenic  $p$  orbital of  $\geq 300$  G, which is certainly greater than the observed linewidth in  $\text{As}_2\text{S}_3$  and is probably inconsistent with the linewidth in  $\text{As}_2\text{Se}_3$ . Hence the holes are probably predominantly localized on either the chalcogens or impurity atoms. For a localized, spin- $\frac{1}{2}$ , paramagnetic center, the deviations of the three principal  $g$  values from the free-electron value  $\Delta g_i$  should scale with the spin-orbit coupling constant  $\lambda$  for the atom on which the center is localized provided that the bonding configurations are equivalent. If the holes are localized on the chalcogen, then  $\Delta g_i$  should scale with  $\lambda$  for S and Se. The value of  $\lambda$  is about 4 times larger in Se than S,<sup>12</sup> and in fact, the values of  $\Delta g_i$  for Se and  $\text{As}_2\text{Se}_3$  are about 3 times greater than those for  $\text{As}_2\text{S}_3$ . It seems unlikely that the observed hole center is directly associated with a paramagnetic chemical impurity in view of the observed composition dependence of the  $g$  value, its agreement with expecta-

tions based on the spin-orbit interaction with the chalcogen, and the observed insensitivity of the  $g$  values to paramagnetic impurity content.

Several experimental facts lead us to associate closely the optically induced absorption and paramagnetism in the chalcogenide glasses with the photoluminescence (PL) observed in these materials: (1) All three effects are characterized by the same excitation band<sup>6,7</sup> ( $\alpha \cong 100 \text{ cm}^{-1}$ ); (2) during continuous excitation both the induced absorption and the ESR intensity grow while the PL efficiency decreases<sup>6,13,14</sup> or "fatigues"; (3) conversely, irradiation with mid-gap light bleaches the induced absorption and the ESR intensity and restores the PL to its cold dark efficiency.<sup>6,13</sup> The obvious suggestion is that radiative recombination centers which become inactive in the PL process during progressive fatigue are associated with the growing ESR intensity and mid-gap optical absorption. Street, Austin, and Searle<sup>15</sup> have described the PL in chalcogenide glasses in terms of holes which form small polarons: Although other specific models cannot be excluded, the present data are consistent with this model.

In summary, we have observed an optically induced ESR at low temperatures in several chalcogenide glasses. An associated induced optical absorption demonstrates that the paramagnetic states are located in the forbidden gap of these amorphous semiconductors. Analysis of the ESR spectra strongly indicates that the paramagnetic centers are holes localized on chalcogens, and are not directly associated with chemical impurities. The study of these optically induced paramagnetic states constitutes a powerful new technique which should provide valuable insights not accessible by other techniques concerning localized gap states in chalcogenide glasses. It remains to be seen whether or not these techniques can be applied successfully to amorphous materials which are not based on chalcogens.

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<sup>1</sup>N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Clarendon Press, Oxford, England, 1971).

<sup>2</sup>D. L. Wood and J. Tauc, *Phys. Rev. B* **5**, 3144 (1972).

<sup>3</sup>H. Fritzsche, in *Electronic and Structural Properties of Amorphous Semiconductors*, edited by P. G. LeComber and J. Mort (Academic, New York, 1973),

p. 55.

<sup>4</sup>S. C. Agarwal, Phys. Rev. B 7, 685 (1973).

<sup>5</sup>F. J. DiSalvo, A. Menth, J. V. Waszczak, and J. Tauc, Phys. Rev. B 6, 4574 (1972).

<sup>6</sup>R. A. Street, T. M. Searle, and I. G. Austin, J. Phys. C: Proc. Phys. Soc., London 6, 1830 (1973), and Phil. Mag. 30, 1181 (1974).

<sup>7</sup>S. G. Bishop and D. L. Mitchell, Phys. Rev. B 8, 5696 (1973).

<sup>8</sup>P. C. Taylor, H. M. Kriz, and J. F. Baugher, to be published.

<sup>9</sup>Low-temperature induced absorption near the band edge (1.4–1.7 eV) in As<sub>2</sub>Se<sub>3</sub> glass has been reported previously: J. Cernogora, F. Molot, and C. Benoît à la Guillaume, in *Proceedings of the Twelfth International Conference on Physics of Semiconductors, Stuttgart, Germany, 1974*, edited by M. H. Pilkuhn (B. G. Teubner,

Stuttgart, Germany, 1974), p. 1027.

<sup>10</sup>F. Stern, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1963), p. 378.

<sup>11</sup>C. M. Hurd and P. Coodin, Phys. Chem. Solids 20, 523 (1966).

<sup>12</sup>P. W. Atkins and M. C. R. Symons, *The Structure of Inorganic Radicals* (American Elsevier, Amsterdam, 1967).

<sup>13</sup>S. G. Bishop and U. Strom, in "Proceedings of the International Conference on the Optical Properties of Highly Transparent Solids, 1975," edited by B. Bendow and S. S. Mitra (Plenum, New York, to be published).

<sup>14</sup>J. Cernogora, F. Molot, and C. Benoît à la Guillaume, Phys. Status Solidi (a) 15, 401 (1973).

<sup>15</sup>R. A. Street, I. G. Austin, and T. M. Searle, to be published.

## High-Spin States in <sup>20</sup>F†

J. N. Bishop\* and H. T. Fortune

Physics Department, University of Pennsylvania, Philadelphia, Pennsylvania 19174

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Results of the reaction <sup>14</sup>N(<sup>7</sup>Li, p)<sup>20</sup>F identify several levels below 5 MeV as candidates for high-spin states predicted by shell-model calculations, but heretofore undiscovered. The 2.97-MeV level is found to be a doublet.

We did this experiment to look for high-spin states, because shell-model calculations<sup>1-3</sup> predict significantly more high-spin states in <sup>20</sup>F than are known<sup>4</sup> experimentally. We made use of

the University of Pennsylvania tandem, multi-angle spectrograph, and Ilford K5 nuclear-emulsion plates with 0.015–0.025-in. Mylar absorber. The target was natural N<sub>2</sub> gas in a windowless

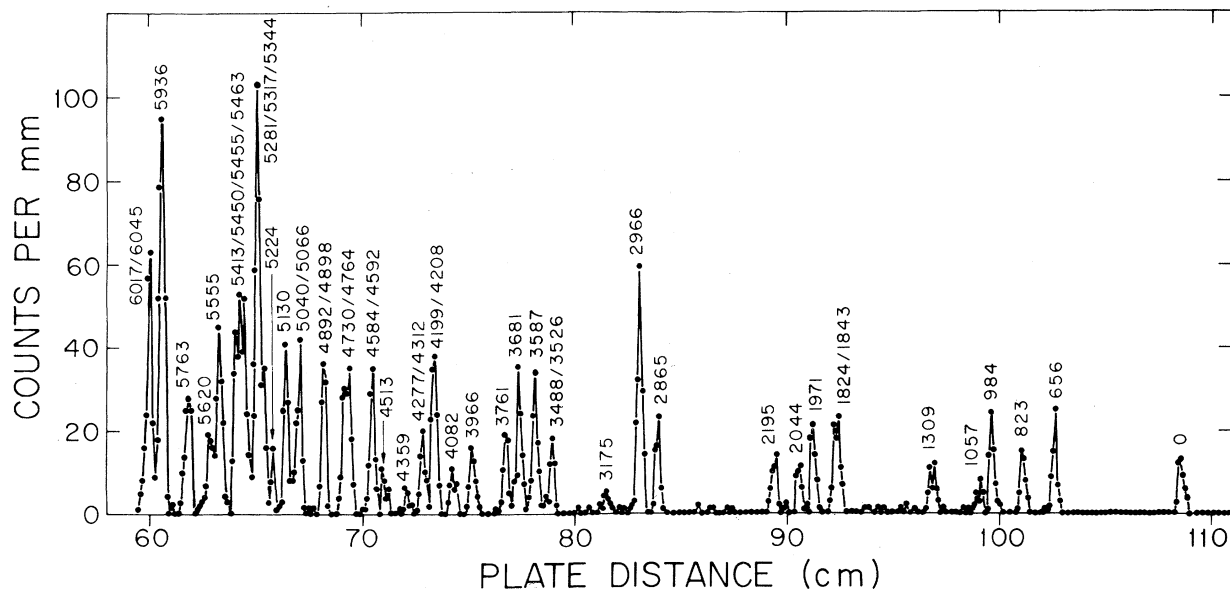


FIG. 1. Spectrum of the reaction <sup>14</sup>N(<sup>7</sup>Li, p)<sup>20</sup>F at 16 MeV and 7½°.