PHYSICAL REVIEW B VOLUME 2, NUMBER 6 15 SEPTEMBER 1970

Evidence for the Role of Excitons in the Production of Paramagnetic Defects in the Azides

Frank J. Owens
Explosives Laboratory, Picatinny Arsenal, Dover, New Jersey 07801

(Received 22 December 1969)

It is found that the ability to produce paramagnetic centers in KN_3 is dependent on the orientation of the $\vec{E}$ vector of polarized ultraviolet light used to produce the damage. The growth rate of the centers is proportional to the square of the intensity of the ultraviolet light. The results are interpreted in terms of excitons being involved in the damage mechanism.

INTRODUCTION

Potassium azide has a body centered tetragonal unit cell. The azide ion is linear and lies in the [110] and the [$1\bar{1}0$] directions of the unit cell.[1] When KN_3 is irradiated with ultraviolet light at 77 °K an N_2^- and an N_4^- paramagnetic molecular ion are produced.[2,3] The mechanism by which the azide ion decomposes is not understood. An investigation has been made of the growth of the ESR of the N_2^- using ultraviolet light. Growth studies were made with the damage producing ultraviolet light polarized with respect to different directions in the KN_3 lattice. The growth of the defect was studied as a function of dosage, time, and intensity of the ultraviolet light. The wavelength of the light necessary to produce the center was determined. The results are interpreted in terms of exciton and impurities interacting to produce the defect.

EXPERIMENTAL

The samples were irradiated at the same time the ESR signal was monitored. The sample was mounted on the end of a quartz rod which was inserted into a liquid-nitrogen quartz finger Dewar. The finger of this Dewar is inserted into an aperture on a microwave cavity of a Varian E-3 ESR spectrometer. Light from a high-pressure mercury lamp was passed through a Corning 7-54 filter in order to remove the visible wavelengths from the beam. The light then passed through an ultraviolet polarizer and through an aperture on the cavity onto the sample. The experimental arrangement is illustrated in Fig. 1.

The KN_3 crystals were grown by slow evaporation of a saturated aqueous solution of potassium azide. A number of samples were cut from one large crystal in such a way that their largest facet was parallel to the (010) plane. When the light beam is directed perpendicular to this facet it is possible to polarize the ultraviolet light perpendicular to all of the azide ions. This arrangement also made it possible to polarize the light with a component parallel to the azide ions. It is not possible to find an orientation of the crystal that allows the light to be polarized parallel to all of the azide ions. Since the ultraviolet light that produces the defect has absorption coefficients of the order of 10^3 cm^{-1}, the defects are produced only in the surface layers of the crystal. Thus, only the area of the facet exposed to the light beam was controlled in size. This was accomplished by masking the facet of the crystal with a screen which had a slit on it. The same screen was used over all different samples. Thus, all samples in which growth rate was compared had the same surface area exposed to light. Comparisons were only made between samples cut from the same crystal. The effect of light intensity was determined by using neutral density filters in the light beam.

RESULTS

In the first part of the experiment, the threshold wavelength for the production of defects was determined. This was done by placing a monochrometer between the lamp and the sample. It was found that defects could not be produced using an irradiation time of 1 h with light of wavelength greater than 2660 Å.

Figure 2 illustrates the two orientations of the $\vec{E}$ vector of the polarized light with respect to the

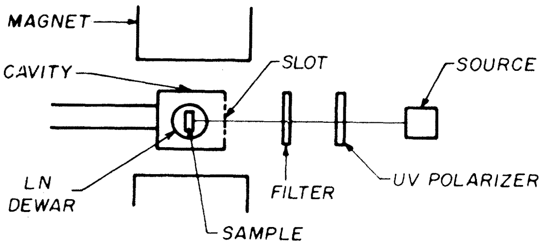

FIG. 1. Experimental arrangement for measuring the growth of the ESR signal of the N_2^- while simultaneously irradiating with uv light.

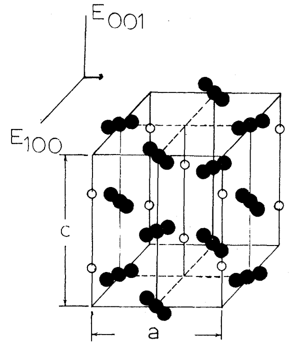

FIG. 2. The unit cell of potassium azide. The two orientations of the $\vec{E}$ vector of the polarized light that were used to measure the growth of the N_2^- are shown.

unit cell of potassium azide for which the growth of the N_2^- radical was measured. The results of the effect of polarizing the damage producing ultraviolet light are shown in Fig. 3. The largest growth occurs when the light is polarized with its $\vec{E}$ vector parallel to the [001] direction. In this direction the $\vec{E}$ vector is perpendicular to all the azide ions. The lesser growth was obtained when the $\vec{E}$ vector of the polarized light was parallel to the [100] direction. This means that the direction of polarization was 45° with respect to each of the two inequivalent azide ions. The growth of the ESR signal of the N_2^- was monitored with the dc magnetic field along the [001] direction of the unit cell.

The data of Fig. 3 yields no information about the shape of the growth curve in the early stages of production. Although a straight line has been drawn between the origin and the experimental point at 40 min, there is no reason to assume that the shape is a straight line. In order to get more detail about this region of the growth curve, the growth of the N_2^- was measured for different intensities and shorter times of irradiation. The typical shape obtained is shown in Fig. 4. The data of Figs. 3 and 4 were taken using different lamps. This was done because the polarizer so reduced the intensity of the transmitted light beam that it was necessary to use a different mercury lamp of higher intensity so that reasonable production rates of the N_2^- could be achieved. The relationship between the intensities of the light incident on the crystal in the two sets of data shown in Figs. 3 and 4 is not known.

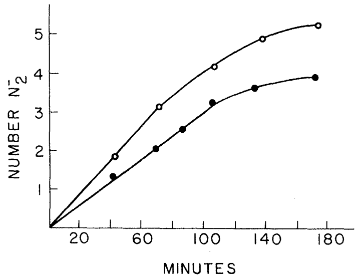

FIG. 3. Plot of the growth of the N_2^- for the two different polarizations of the damage producing uv light. The top curve is obtained for the $\vec{E}$ vector parallel to [001] of the lattice. The lesser growth is obtained when the $\vec{E}$ vector is parallel to the [100] direction.

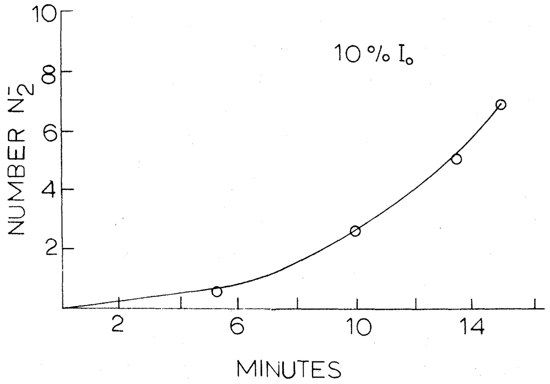

FIG. 4. A plot of the growth of the N_2^- versus time showing more detail in the early region of the curve. The numbers on the vertical axis of Figs. 3 and 4 are arbitrary and bear no relationship to each other as different uv sources were used in both sets of data.

INTERPRETATION

In unirradiated KN_3 there exists an optical absorption band at 2250 Å containing what appears to be vibrational structure on it. The band has been attributed to a low-lying excitation of the azide ion.[4] Similar bands are seen in the solutions of the inorganic alkali azides as well as in the crystals.[5] Thus, the association of the band with a transition in the azide ion seems reasonable. The band has been observed to be dichroic with the greatest absorption occuring when the $\vec{E}$ vector of the absorbed polarized light is perpendicular to the plane of the azide ions.[6]

The fact that it is found that to produce the N_2^- it is necessary to irradiate into this band, and the similarity of the dichroic properties of the 2250-Å band to the polarization effect on the growth of the N_2^- suggest that the excited state that is responsible for the band is the same excitation that is involved in the damage mechanism. However, the dichroism alone of this transition is not sufficient to explain the difference in the growth of the N_2^- with polarization. Since the absorption coefficient of the crystal is high in the ultraviolet part of the spectrum, all the quanta are absorbed in the surface layers of the crystal. The absorption coefficient is greater for [001] polarization than for [100] polarization of the light. However, in both cases the same number of azide ions will be excited. In the case of the [001] polarization the density of excited azide ions will be greater. If the decomposition of the azide ion occurred immediately upon excitation and was a process independent of other excited azide ions, then the same number of N_2^- defects should occur for both polarizations. The fact that this does not happen suggests that the ability of the azide ion to decompose after excitation is dependent on the density of the excited azide ions. Such a process could require that the excitations be mobile and that decomposition occur only when two or more excitations come into the vicinity of each other. In the more dense region of excitations there would be a greater probability for this to occur.

If the decomposition of the azide ion is dependent on the density of excited azide ions, then it should follow that the growth of the N_2^- will have a nonlinear dependence on intensity. An attempt has been made to determine the dependence of the growth of the N_2^- on intensity. In order to do this it is necessary to construct a model for the damage mechanism. The result of the model would be to yield an equation for the growth of the N_2^- as a function of the time and intensity. This equation would then be fitted to the data and the intensity dependence abstracted. At present there is insufficient data to allow a complete detailed model of the production process to be constructed. Nevertheless, a simple approximate model based on available data will be suggested to explain the early stages of the growth process. The main purpose for doing this is to demonstrate that the growth of the N_2^- is not linearly dependent on the intensity of the ultraviolet light. The qualitative shape of the growth of the N_2^- with time suggests some ideas about the mechanism of the growth of the center. First, it is noted that there is an initial slow growth stage followed by a stage in which the rate of growth increases considerably. This indicates that before the center can grow at an appreciable rate, some other intermediate defect has to be first produced. Further, it is noted that the growth of the N_2^- appears to saturate; i.e., the rate of growth of the center becomes zero. It should be noted that there are other paramagnetic centers in KN_3 such as the N_4^- which continue to grow after the N_2^- has saturated. A possible explanation for the saturation is that an impurity is playing a role either in the production of the center or is necessary for the stabilization of the defect. It has been observed that the growth rate of the N_2^- is less in crystals which are purer. In particular, the presence of nitrate impurities in the crystal enchances the growth of the N_2^-.

A plot of the relative number of defects versus the square of the time for the different relative intensities of the ultraviolet light is shown in Fig. 5. The lines are obtained by using data only from the early stages of the growth well below the saturation region. This time dependence can be explained on the following simple model. Assume that the rate of growth of the N_2^- is proportional to the product of the number of intermediate defects $[N_x]$ and the number of excited azide ions. There is no evidence to indicate that the intermediate species that appears necessary before any appreciable growth of the N_2^- occurs is the same as the impurity that can cause the saturation. By writing the rate of production as the product of the number of intermediates and the number of excited azide ions it is implied that an intermediate species and an excited azide ion have to interact before a dissociation of the azide ion can occur. The probability for this to happen would depend on the density of the excited azide ions as is suggested by the polarization effect in the growth of the N_2^-. If the number of excited azide ions is taken as proportional to the intensity I, then

$$\frac{d[\mathrm{N}_2^-]}{dt} = k[\mathrm{N}_x]I \; . \tag{1}$$

Take

$$\frac{d[\mathrm{N}_x]}{dt} = aI \; . \tag{2}$$

The combined solution of these yields

$$[\mathrm{N}^-{}_2] = cI^2t^2 , \tag{3}$$

where $c = ka/2$.

The above model, which is only applicable in the region of the growth curve well before saturation, predicts that the growth of $[N_2^-]$ is proportional to the square of the intensity and the square of the

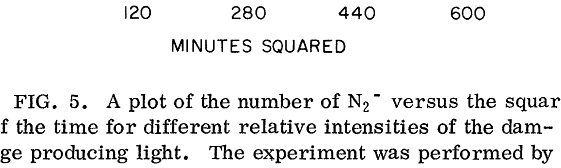

FIG. 5. A plot of the number of N_2^- versus the square of the time for different relative intensities of the damage producing light. The experiment was performed by placing neutral density filters between the source and the crystal. The I_0 refers to the intensity of the unfiltered light.

time. A plot of the slopes of [N_2^-] versus time squared lines against the square of the intensity yields a straight line as predicted by this model. This plot is shown in Fig. 6. Thus this simple model appears to explain the nature of the growth in the initial stages of the production of the center. The point of this analysis is not to suggest a definitive model for the production process, but rather to provide an argument that the growth of the center is not linearly dependent on intensity. This nonlinear dependence provides further support for the idea that excitons are involved in the production of the N_2^- as suggested by the polarization experiment. It is interesting to note that the rate of evolution of nitrogen gas from the crystal has been observed to be proportional to the square of the intensity of the damage producing uv light.[7]

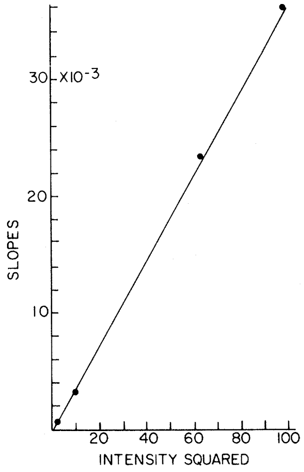

FIG. 6. Plot of the slopes of the lines of Fig. 5 versus the square of the relative intensity of the ultraviolet light.

CONCLUSION

The results of the experiment yield some insight into the mechanism by which uv light decomposes potassium azide. It has been established that the first step in the process involves the light exciting the azide ion and that this excitation is the same one that gives rise to the 2250-Å optical absorption observed in all the azides. The polarization effect in the growth of the centers and the nonlinearity of their growth with the intensity of the uv light suggests that the ability of the azide ion to decompose is determined by the density of the excitations. Production of excitons with dissociation of the ion when two or more excitons are in the vicinity of each other would explain the result. However, it appears more likely from the shape of the growth curve that the process involves an exciton and an impurity associated defect, or some other intermediate defect.

ACKNOWLEDGMENTS

The author would like to acknowledge many fruitful discussions with Dr. R. Bartram of the University of Connecticut, Dr. N. Geacintov of New York University, and Dr. D. Wiegand, Dr. J. Sharma, and Dr. T. Gora of the U. S. Army Explosives Laboratory.

---

[1] T. C. Waddington, J. Chem. Soc. 2499 (1959).

[2] A. J. Shuskus, C. G. Young, O. R. Gilliam, and P. W. Levy, J. Chem. Phys. 33, 662 (1960).

[3] R. B. Horst, J. H. Anderson, and D. E. Milligan, J. Phys. Chem. Solids 23, 157 (1962).

[4] S. K. Deb, J. Chem. Phys. 35, 2122 (1961).

[5] I. Burak and A. J. Treinin, J. Chem. Phys. 39, 189 (1963).

[6] L. Bogen (private communication).

[7] P. W. M. Jacobs and F. C. Tompkins, Proc. Roy. Soc. (London) A11, 254 (1952).