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ESR Measurement and Irradiation at Variable Temperatures below 77°K

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An apparatus for irradiation and subsequent ESR measurements at variable temperatures below 77°K was constracted by combining an ESR spectrometer, and an X-ray irradiator, and a laboratory scale low temperature refrigerator operating at the temperature region between 77 and 4.2°K. A device for rotating the single crystal specimen was made to measure the angular dependence of the ESR spectra. The lowest specimen temperature achieved was estimated to be 6°K and the precision of the temperature control was less than ±0.5°K for a period of several hours. The apparatus makes it possible to irradiate samples and to measure ESR spectra at any temperature in the range between 77 and 6°K. Some applications for irradiation and ESR measurements at low temperatures are also described. An unstable radical which disappears at about 60°K was found in an irradiated single crystal of L-cystine dihydrochloride. Experimental evidence for the quantum tunnelling of the methyl group in polymethylmethacrylate radical was also found by the temperature dependence of the spectra observed at temperatures lower than 77°K.

ESR measurements at a temperature region lower than 77°K are usually carried out at 4.2°K by using liquid helium. In some cases, even lower temperatures can be achieved by rapid pumping of liquid helium. It is not easy, however, to maintain intermediate temperatures between 4.2 and 77°K (liquid nitrogen temperature), especially for a fairly long period. For example, in the measurements of the orientation dependence of the ESR spectra of single crystals, a constant temperature with a fairly high precision has to be maintained for at least several hours. In addition, for the study of the primary process of radiation-induced reactions, the irradiation is to be made at temperatures lower than 77°K, because of instability of the produced radicals. This kind of experiment can not be easily carried out by using liquid helium. Besides, liquid helium is not always available and is not easy to handle. If low temperatures could be obtained without the use of liquid helium, a number of laborious processes required for experiments at a temperature region lower than 77°K might be considerably reduced.

Recently a laboratory scale refrigerator which can be operated by using a compressed helium gas from commercial cylinders has been developed and it provides a fairly simple way to obtain any intermediate temperatures between 77 and 4.2°K. We have applied

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this sort of equipment for irradiation and subsequent ESR measurements at low temperature and obtained fairly successful results. This paper describes our apparatus built mainly for the measurements of the angular dependence of the ESR spectra of irradiated single crystals.

In this method the crystals are cooled by thermal conduction through the contact with a cryogenic tip of the refrigerator so that a number of checks have to be made to ascertain the real temperature of the specimens. Performance of our equipment will be described together with some results obtained for the NO radical in a single crystal of hydroxylamine hydrochloride, irradiated single crystals of *N*-acetylalanine and L-cystine dihydrochloride, and irradiated polymethylmethacrylate films.

Apparatus

The refrigerator is a Cryo-Tip system AC-3L-110 supplied by Air Products and Chemicals Inc. The alignment of an ESR spectrometer, X-ray irradiator, and the refrigerator is shown in Fig. 1. The movable mount of the refrigerator was designed and built to make it possible to shift the refrigerator horizontally from the X-ray irradiator to the sample cavity for prompt ESR measurements after irradiation. Besides this horizontal movement, the mount performs vertical movement for inserting the specimen holder into the X-ray irradiator or the sample cavity, and the rotational movement for changing the crystal orientations to the magnetic field. The mount has also a cross leader for the fine adjustment of the sample position in the cavity. A device for adjusting the vertical axis of the refrigerator is also added to make sure that the rotational axis of the crystal is perpendicular to the magnetic field. A sketch of the refrigeraaor mount is shown in Fig. 2.

Hydrogen and helium gases from cylinders are led to the liquid nitrogen dewar where the gases are precooled down to 77°K. Hydrogen and helium gases are then expanded successively and liquefied at the tip

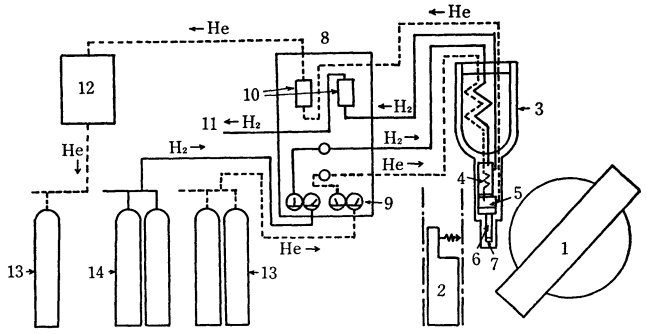

Fig. 1. Block diagram of the apparatus for irradiation and subsequent ESR measurements at variable temperatures lower than 77°K: 1. ESR magnet; 2. X-ray tube; 3. liquid nitrogen Dewar; 4. hydrogen liquefying chamber; 5. helium liquefying chamber; 6. specimen holder; 7. specimen; 8. control panel; 9. pressure regulator; 10. flow meter; 11. vent for hydrogen gas; 12. apparatus for restoring helium gas; 13. helium cylinder; 14. hydrogen cylinder.

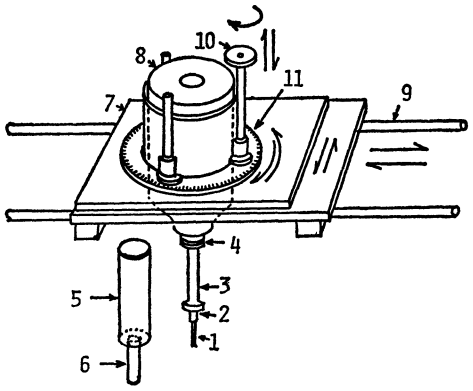

Fig. 2. Sketch of the refrigerator and its movable mount: 1. specimen holder; 2. heat exchanger; 3. radiation shield; 4. O-ring for vacuum shroud; 5. vacuum shroud; 6. spectrosil tube; 7. refrigerator holder; 8. Dewar vessel of liquid nitrogen; 9. guide rail for horizontal shift; 10. handle for vertical shift; 11. indicator for rotational angle. Although the mechanisms are not shown in the figure, the positions in the horizontal plane are adjustable to two perpendicular directions by fine adjustment knobs. The vertical axis for rotation is also adjustable.

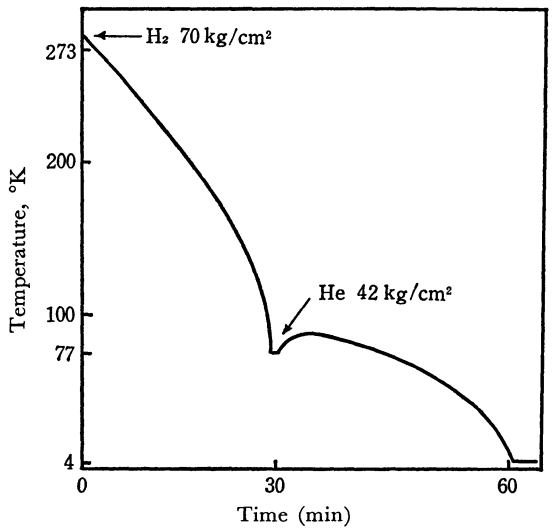

Fig. 3. Cooling curve for normal operation of the refrigerator.

of the refigerator. Figure 3 shows a cooling curve measured with a chromel-constantan thermocouple attached to the tip of the refrigerator. After the low pressure purge at 7—14 kg/cm² for 20 min, the hydrogen pressure was raised to 70 kg/cm². This is taken as an origin of the time scale in the abscissa of Fig. 3. After 30 min needed for liquefying hydrogen gases, the hedlium pressure was increased to 42 kg/cm² and another 30 min were required to liquefy helium gases. The tip temperature is easily controlled in the range from 77° to 4.2°K by adjusting the flow rate of the gases. It is easy to maintain any intermediate temperature, say 40°K, for several hours with an accuracy of less than ±0.5°K.

A vent pipe of the used hydrogen gas is led to the roof, while the helium gas is restored to the cylinders by a compressor through a liquid nitrogen trap with

active charcoal.

Specimens for ESR measurements are attached to the sample holder of a sapphire or a copper rod (3 mm$\phi \times$80mm) connected to the tip of the refrigerator surrounded by an aluminum vacuum shroud (Fig. 2). The length of the specimen holder depends on the dimension of the ESR cavity into which part of the specimen holder is inserted. The part of the specimen holder is surrounded by a Spectrosil tube of 10 mmϕ, the inside of which is evacuated through the vacuum shroud for maintaining thermal insulation. The ESR measurements are easily carried out by inserting the Spectrosil tube into a cavity with a TE_{011} mode. Adjustment of the orientation of the specimen to the magnetic field can be achieved by simply rotating the refrigerator mount around the vertical axis. This method is entirely free from the bubble noise inherent to the method using liquid coolants. Since the surface of the Spectrosil tube is maintained at room temperature, there is no variation of the Q-value of the sample cavity even though the temperature of specimen changes.

Irradiation of the specimen at low temperatures is also easily carried out by inserting the Spectrosil tube into the irradiation chamber in which an X-ray tube is installed The X-ray irradiator is placed in front of an ESR magnet at a distance of about 1 m to make it easier to transfer the refrigerator promptly to the ESR cavity right after irradiation. The ESR signal due to color centers produced at room temperature in the Spectrosil tube by X-irradiation is a sharp singlet having the g-factor close to the free spin value and its intensity is not so strong that the central part of the signal of the specimen is masked.

Temperature Measurements

Although the temperature of the tip of the refrigerator is maintained at 4.2°K when helium gas is liquefied, there should be thermal gradient along the rod of the specimen holder in such a way that the specimen is cooled by the thermal conduction through a long rod. The temperature difference between the tips of the refrigerator and the sapphire or copper rods measured by an Au doped Co–Pt thermocouple was about 6 and 4°K, respectively, when the Cryo-Tip system was operated with full power. The temperature rise through the rod is reduced to 2—1°K when the temperature of the tip of the refrigerator is raised to 70°K. Figure 4 shows the correction curve for the temperature rise at the sample position of the rod. The ordinate represents the temperature rise through the rod and the abscissa the temperature at the tip of the refrigerator.

The main cause of the temperature rise through the rod seems to be the radiation from the Spectrosil tube which is kept at room temperature. The vacuum in the Spectrosil tube is extremely high because the residual air is completely trapped on the surface of the heat exchanger, the temperature of which is very much lower than the freezing points of oxygen and nitrogen. Therefore, the conduction through the residual gases from the Spectrosil tube may be negligible. It is not possible, however, to use a radiation shield of silver mirror inside the Spectrosil tube as in the Dewar vessel because it lowers the Q-value of the sample cavity. When the Spectrosil tube was dipped into a liquid nitrogen dewar, the temperature rise became negligibly small and the liquid helium temperature was attained. Therefore, the cold nitrogen gas from the Dewar vessel of liquid nitrogen was introduced into the sample cavity to lower the temperature of the surface of the Spectrosil tube. By this device the temperature rise through the rod is reduced to about 2°K when the copper rod is used at the full operation of the refrigerator. The lowest possible specimen temperature obtained by our apparatus is about 6°K.

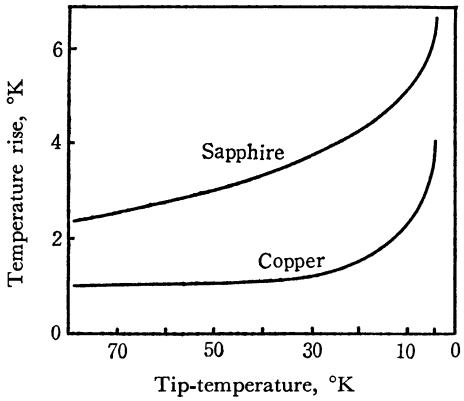

Fig. 4. Correction curve for the temperature rise along the sample rod *vs.* temperature of the cryogenic tip of the refrigerator.

The temperature rise during X-irradiation was found to be 2—3°K under operating conditions of 30 mA and 40 kV. The distance from the X-ray target to the specimen holder is about 30 mm.

The temperature of the sample itself attached to the rod is very difficult to measure, because of the small size of the crystal or film. In order to avoid the thermal gradient inside the specimen, it is necessary to use a very thin, say 0.1—0.2 mm, crystal or film. In this case, the temperature of the sample was confirmed by the ESR measurements.

ESR Measurements

According to Gamble and Miyagawa, the ESR spectrum of the radical CH_3–$\dot{C}R_1R_2$ formed in an irradiated single crystal of *N*-acetylalanine shows a remarkable temperature dependence in the region between 4—20°K due to the quantum mechanical effect on the hindered oscillation of methyl group.[1] Temperature changes of the spectral features they observed at 4.2, 12.5, and 17.5°K are so sensitive to the observed temperature that it may provide a good test sample for checking the real temperature of the specimen. We have also measured the temperature dependence of the same sample by using our apparatus with a copper rod as a sample holder. The spectra obtained at 12.5 and 17.5°K, which were estimated from the correction curve in Fig. 4, are in very good

1) W. L. Gamble and I. Miyagawa, *Phys. Rev. Lett.* **20**, 415 (1968).

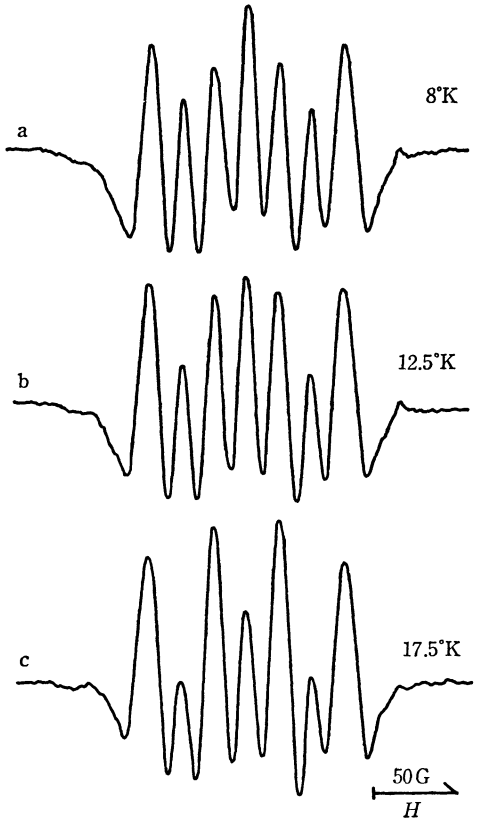

Fig. 5. ESR spectra of an irradiated single crystal of *N*-acetylalanine measured at (a) 8°K, (b) 12.5°K, and (c) 17.5°K. The magnetic field is applied along the *c*-axis.

agreement with their spectra as shown in Figs. 5(b) and (c). This means that the specimen temperature is practically the same as that of the copper rod. Figure 5(a) gives a spectrum observed at 8°K which is the lowest temperature obtained by our apparatus without aid of cold nitrogen gas flow into the sample cavity. The spectral feature of Fig. 5(a) is in between their spectra observed at 4.2 and 12.5°K. The splendid agreement between the two independent measurements may ensure the estimates of the specimen temperature in both the experiments.

In the temperature region higher than 20°K, the spectral change of this radical is so gradual that it is of no use to check the specimen temperature. Therefore another check was made by using the Curie law, *viz.*, the linear relation of the ESR intensity to reciprocal temperature. For this purpose one has to use the sample, the signal of which is hard to saturate at the low temperature region. The NO radical found by Ohigashi and Kurita[2] in an irradiated single crystal of hydroxylamine hydrochloride has extremely short T_1 and it may be expected that the signal is not saturated in a fairly wide range of low temperature. Figure 6 shows the relative intensity of the ESR spectra of the NO radical plotted against the reciprocal temperature estimated from the correction curve in Fig. 4. In this experiment, the sapphire rod was used for the specimen holder. As is seen in Fig. 6, a good linear relation was obtained in the temperature range between 25 and 60°K.

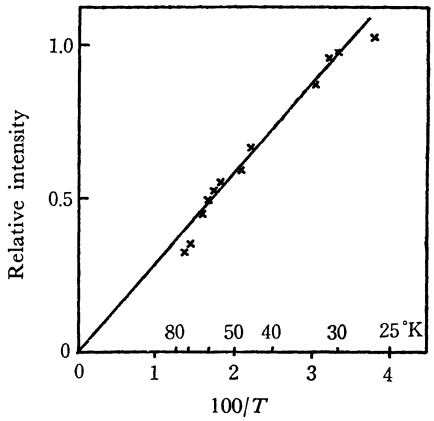

Fig. 6. Plots of the ESR intensities *vs.* reciprocal temperatures for the NO radical trapped single crystal of hydroxylamine hydrochloride.

It is concluded that the specimen temperature is practically the same as that of the sample rod in the wide range of low temperature achieved by our apparatus.

Applications

Irradiation at low Temperature. In some cases irradiation has to be made at temperature lower than 77°K, since the primary species produced by irradiation are sometimes unstable at 77°K. For example, the cation radical formed in an irradiated single crystal of L-cystine dihydrochloride[3] is known to be unstable at 77°K.[4] Irradiation at temperatures lower than

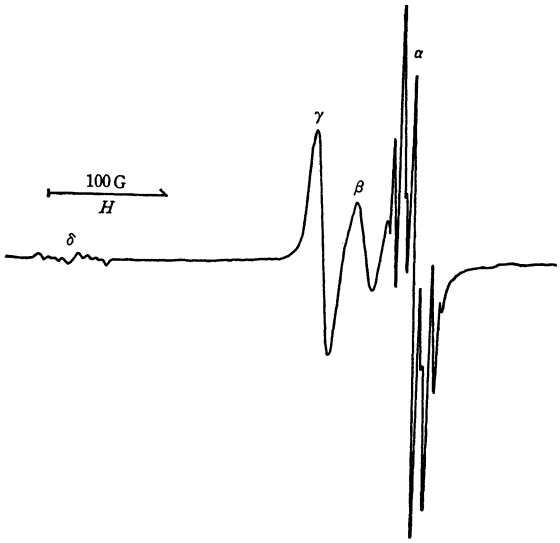

Fig. 7. ESR spectra of a single crystal of L-cystine dihydrochloride irradiated and measured with our system. The magnetic field is applied along the *c'*-axis.

2) H. Ohigashi and Y. Kurita, *J. Phys. Soc. Jap.* **24**, 654 (1968).

3) H. C. Box, H. G. Freund, K. T. Lilga, and E. E. Budzinski, *J. Phys. Chem.*, **74**, 40 (1970).

4) According to the recent study of Akasaka *et al.* (13th Symposium on Radiation Chemistry, Tokyo, Oct. 9, 1970), the spectrum of the cation is observable even at 77°K if the observation is made in the dark.

77°K is desirable for studying the primary process of radiation-induced reactions.

Our system was applied in the irradiation of a single crystal of L-cystine dihydrochloride. A typical spectrum measured right after irradiation is shown in Fig. 7. Both the cation (α in Fig. 7) and the anion (β in Fig. 7) are stably trapped. In addition, a new signal δ with an extremely large g-anisotropy and a small hyperfine structure was found at lower magnetic field side of the spectra due to the cation and anion. The signal disappeared irreversibly when the temperature was elevated to about 60°K. Figure 8 shows an angular dependence of this signal measured in the ac′ plane. The variation of the g-value in this plane is from 2.26 to the free spin value. Although the magnetically non-equivalent site of this signal is one in the ac' plane, there are two sites in both the ab and bc' planes. This means that the radical responsible to this signal does not possess symmetry of the mother molecule. From this together with the large positive g-shift the signal may be assigned to a sort of sulfur radical produced by the scission of the S–S bond.

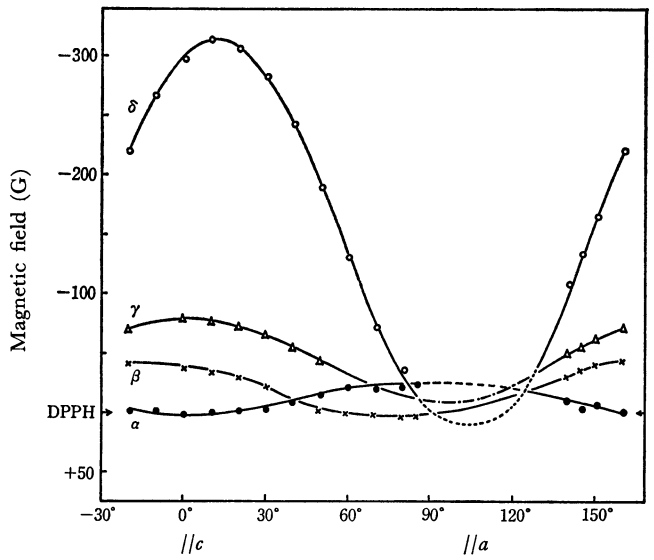

Fig. 8. Angular dependence of the ESR spectra of a single crystal of L-cystine dihydrocholide irradiated and measured with our system. The magnetic field is applied in the ac′ plane.

This experiment shows that our system is applicable to the irradiation at temperatures lower than 77°K and the subsequent ESR measurements.

Measurements of ESR Temperature Dependence. In some cases, the temperature dependence of the ESR spectra in a temperature region lower than 77°K is required to be measured. As an example, it is reported that the ESR spectrum of polymethylmethacrylate radical, RCH_2–$\dot{C}(CH_3)COOMe$ measured at 4.2°K exhibits a remarkable difference from that at 77°K.[5] Interpretation of this difference is not possible because of the lack of information on the spectral change at intermediate temperatures. By means of our system the temperature dependence of the spectra was successfully measured in the range between 77 and 6°K. The results are shown in Fig. 9. As described in our paper,[6] the spectrum observed at 77°K is interpreted on the assumptions of the freely rotating methyl group and the distribution of the conformational angle of the two C–H_β bonds to the half filled $2p$ orbital. The spectral change observed at temperatures lower than 77°K can be interpreted by the quantum mechanical effect on the hindered oscillation of the methyl group as is the case of the radical, CH_3–$\dot{C}R_1R_2$, in irradiated *N*-acetylalanine.[1] The spectra observed at 6°K is well reproduced by the seven-line spectrum due to the quantum tunnelling of the methyl group[7] and further splittings due to the two β-proton couplings. The temperature dependence observed by our system gave the experimental evidence for the quantum tunnelling of the methyl group in the polymethylmethacrylate radical. Details will be given elsewhere.

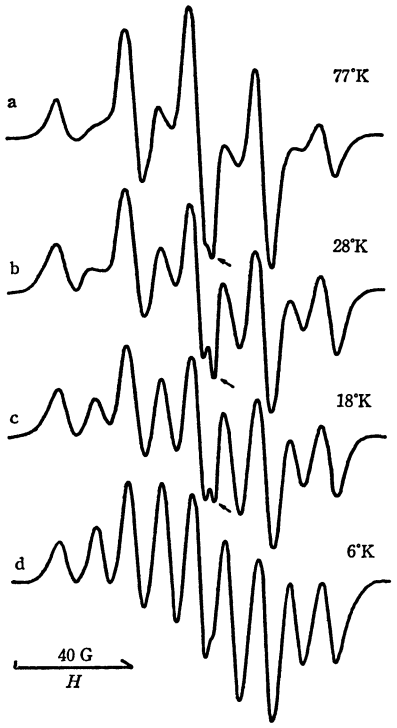

Fig. 9. Temperature dependence of the ESR spectra of polymethylmethacrylate radical measured at (a) 77°K, (b) 28°K, (c) 18°K, and (d) 6°K. The arrows indicate the signal due to the color center of the Spectrosil tube.

The authors wish to thank Drs. Y. Kurita and H. Ohigashi of Basic Research Laboratory, Toray Industries, Inc. for their helpful cooperation in measuring the ESR signal of the NO radical trapped in an irradiated single crystal of hydroxylamine hydrochloride.

5) D. W. Ovenall, *Nature*, **184**, 181 (1959).

6) M. Iwasaki and Y. Sakai, *J. Polymer Sci.*, *A*-1, **7**, 1537 (1969).

7) J. H. Freed, *J. Chem. Phys.*, **43**, 1710 (1965).