Northeastern University

Boston, Massachusetts

Quarterly Progress Report #2

Covering the Period August 16, 1969-November 15, 1969

NASA Grant No. NGL 22-011-051

Submitted by

Clive M. Perry

Prepared for National Aeronautics & Space Administration
Office of Scientific & Technical Information (Code US)
Washington, D.C. 20546

Quarterly Progress Report #2

on

The Study of Optical Properties and Collective Oscillations

in New Solid State Materials and as a Function of Temperature

Using Infrared and Raman Techniques

Work Accomplished and in Progress

1. Instrumentation

Some electronic difficulties have been experienced with both interferometers but these have now been solved and they are now back in operation. Both Golay detectors had to be replaced. The FS-720 is being used successfully with the high pressure diamond cell and the thallium halides (especially the phase change in TlI) are under investigation.

The laser Raman instrument is under major modification. The new double monochromator is awaiting delivery from Spex Industries and will have a linear wavenumber drive. This will allow more convenient calibration with different laser lines. The source optics is being completely re-designed to allow for the additional scattering geometries of forward and backward as well as right angle. Acceptance of liquid helium cryostats and high pressure cells will be accommodated with the minimum amount of inconveniences. Shielding of the He-Ne laser is necessary as the R.-F. discharge upsets other experiments in the Solid State Group.

The Kramers-Kronig program has been completed by Dr. Parrish before he left and allows for calculation of the real and imaginary parts of the dielectric constant and conductivity. It will accept reflectivity data for any angle of incidence and is about to be tested out experimentally and analytically.

3. Variable Temperature (8-400°K) Gas Transfer Cell for Solid State Spectroscopy. (M.E. Tormberg and C.M. Parry)

Introduction

Many intensive studies that involve Raman spectroscopy as an observational tool also require the control and variation of temperature. A common spectrophotometer used in such work is the Cary model 81 with He-Ne laser excitation. In that instrument, the laser beam is directed at the sample from overhead, rendering the use of usual dewar design impractical if not impossible. Although long term precision control of the temperatures attained was not deemed necessary in the authors' work, it was desired that the entire range from 300° to somewhat below 20°K be attainable without changing critical sample illumination geometries. Also, it was considered worthwhile that sample changing be quick and convenient and thus that temperature cycling be fairly rapid within the above range. It was felt that the best means of dealing with these requirements and restrictions was through the use of a cell which achieved temperature control by means of precooled or preheated gas directed at a metal block in thermal contact with the substance under study. The design presented here resulted from these considerations.

Cell Design

The cell consists of four principle elements which are shown in Fig. 1. Element I is a modified transfer tube with an expanded outer jacket at the interface with the rest of the system to which an "O" ring seal is effected. About this expanded section is a ring with a longitudinal slot which may be clamped to the jacket by tightening a screw traversing the slot. This ring acts as a stop to hold the end of the transfer tube a predetermined distance from the back of the sample block.

Element II consists, in sequence, of the above-mentioned "O" ring seal assembly, radial vent holes distributed about its circumference to release spent coolant gas, a short section of tube to mate with the "O" ring seal in element III, and a concentric inner tube which supports the copper sample block. The outer tubular section serves as a portion of the outer vacuum jacket and the copper sample block features a ¼ x 20 threaded hole on its sample face to accept the actual sample holder. Part way back from the sample block a copper collar is mounted on the tube on which a radiation shield which encloses the sample area may be mounted by a snug force-fit. Electrical leads may be led into the sample area by means of a slot in the collar. This collar, and thus the shield, are cooled by the exiting coolant, which also serves to cool the outer case of the transfer tube. Another slotted ring clamp surrounds the outer concentric tube to establish the longitudinal location of the sample area within the cell.

Element III serves as a mount for a pump-out port and for electrical feedthroughs into the sample area. It also connects the preceding portions of the cell to the tail portion of the vacuum jacket. This element consists, in sequence, of the "O" ring seal assembly for element II, the electrical feedthrough assembly on a demountable flange and opposite this a pump-out port including a valve to isolate the cell, and an "O" ring seal assembly to join to the tail vacuum jacket.

Element IV is the tail section vacuum jacket. This consists simply of a tube terminated at one end with a rectangular block containing ports, "O" ring seals, and mounting provision for windows of quartz or other material.

Cell Use

Temperatures up to approximately 130°C could be obtained by replacing element I (modified transfer tube) with a porcelain tube around which a nichrome heater was wrapped and through which the gas was passed. Since elevated temperatures could be obtained more easily by other means, however, heated air (or nitrogen) was used primarily to warm up an already cold cell if condensation on the sample was to be avoided. Cold gas was obtained in one of two ways. First, nitrogen was passed through a copper coil immersed either in a dry ice-acetone solution or in liquid nitrogen. Second, an approximately 10 ohm wirewound resistor powered by a commercial 25 v, 5 amp variable power supply was used to boil liquid helium. A modified tip on the transfer tube accepted the gas above the liquid, passed it through an outer tube to the tip's end near the bottom of the dewar and hence through an inner tube to the transfer tube proper.

A standard Janis Research Co. flexible transfer tube was used for the helium gas. One end was modified by being shortened and given an expanded jacket as indicated above. The tube used for nitrogen was merely the expanded jacket and short vacuum-insulated tip since the cold temperature bath was commonly placed near the cell and a short piece of insulated hose connected the copper coil in the bath to the cell.

Although the design included provisions for partial temperature control by adjusting the distance from the transfer tube outlet to the back of the sample block, it was found that this did not have a usefully large effect within the range of movement possible (~ 2½"). Thus, all temperature control was achieved by controlling gas temperature and flow rate. In Fig. 2 are data representing the average conditions encountered in attempting to

maintain low temperatures with cold helium gas. Convenient control could be obtained in the region 20°-50°K without the shield and 8°-25°K with it. Within these regions temperature could be stabilized within ±0.2°K for periods of 30 minutes or more. The large copper block damped temperature fluctuation due to variations in gas flow with an estimated time constant of from 2 to 5 minutes, depending on temperature. The radiation shield mounting collar was about 5 3/4" from the sample area and at lower sample temperatures the shield operated at from 60 to 65°K.

At higher temperatures the radiation shield still had some effect. With it installed temperatures from essentially that of liquid nitrogen could be obtained using nitrogen cooled in a bath of the liquid gas; without it, required gas flow was too small for good control at about 120°K.

Using dry ice-acetone as the cooling bath, temperatures from 200°K could be obtained by regulating gas flow alone.

Temperatures above the indicated ranges for helium- or nitrogen-cooled transfers could be easily attained. However, the small gas flow required rendered control somewhat uncertain with the result that long term stabilization to better than ±2°K could not be obtained. In the case of liquid nitrogen cooling, this could easily be circumvented by a less efficient heat exchanger in the bath or a heater on the transfer tube. For liquid helium cooling, a heater could easily be mounted in the sample area for dynamic heat flow balance at higher temperatures. In both cases, exact temperature control was not required by the authors in the ranges indicated so these modifications were not effected.

In general use, it was found that temperature cycling could be made quite rapid. The transition from 300° to 20°K could be made in about 10

minutes, with the warmup using heated air requiring about the same length of time.

Controlled, slow temperature sweeps were also quite easily accomplished permitting detailed examination of the effects of phase transitions on the spectra.

Mechanically, the cell proved quite convenient to use. The tail jacket was clamped into the sample - illuminating chamber of the spectrometer by a slotted ring mounted on its case. The cell itself was supported by a pair of chain clamps mounted on an optical rail aligned with the optic axis of the Cary spectrometer. This permitted the cell (without tail vacuum jacket) to be quickly extracted from the spectrometer by sliding its mounts along the rail. It would then be very easily returned to its previous configuration. Sample orientation could be accomplished quite easily because of the longitudinal and rotational degrees of freedom. Also, the transfer tube portion could be removed without significantly disturbing the remainder, thus permitting operation over the entire attainable temperature range without attention to optical alignment. The cell could easily be configured for various sample illumination geometries by providing various tail jackets - relatively small pieces to make. Considerable frost would build up about the gas vents but did not prove a problem. Stainless steel was used exclusively except for the copper portions with the result that the cold portions of the case were quite localized due to the poor heat conduction.

Further Applications

The success of the cell as specifically applied to studies involving the Cary instrument, along with its small size, light weight, easily changed geometry, and insensitivity to operating position, suggested its usefulness

in a wide variety of applications. It was easily adapted for use with the Spex double monochromator with laser excitation since it could, with a minimum of external support, be mounted vertically on the lid of the sample illuminator supplied as an option with that instrument. Its operation in that configuration did not vary significantly from that described above. Operated vertically, it could also be used as a conventional dewar for liquid nitrogen and warmer baths. The hold time for the small quantity of liquid nitrogen it would contain proved to be approximately 40 minutes, generally adequate for spectroscopic work.

The cell's versatility was extended to infrared investigations by using CaF and polyethylene windows, either on the same tail vacuum jacket or on another. In this configuration it has been used in transmission with Perkin Elmer models 301 and 521 grating instruments, and Beckman models FS 720 and FS 520 Michelson interferometers. With the latter it has also been used in reflection, its quick temperature cycling allowing rapid change between the two, since multiple tail jackets can be mounted at different locations in the sample chamber. The cell also has been used successfully with an evaporator attachment for first obtaining thin films in situ and then, by rotating the cell 90° within the vacuum jacket, taking direct infrared transmission measurements.

This cell has been employed in several solid state spectroscopic investigations, the results of which appear elsewhere in the literature.[1-4]

References

1. C. H. Perry and H. E. Tornberg, Phys. Rev., 10 July, 1969 (in print).

2. M. E. Tornberg and C. H. Perry, Solid State Comm. 6, XVI (1968) and in Conference on Light Scattering Spectra of Solids, ed. G. B. Wright (Springer-Verlag, New York, 1969), paper F3, pp. 467, 476.

3. C. H. Perry and R. P. Lowndes, J. Chem. Phys. 51, October (1969).

4. R. P. Lowndes and C. H. Perry, paper T5, Molecular Spectroscopy Symposium, Ohio State University, Columbus, Ohio, Sept. 2-6, 1969, p. 88.

Figure Captions

Fig. 1 Simplified mechanical drawing of temperature-control cell.

A Transfer tube out to supply of refrigerant gas.

B Omission of 1 3/8" of material.

C Omission of 2" of material.

D Tube out to vacuum feedthroughs on demountable flange.

E Tube out to valve and evacuation line.

F Omission of 4½" of material.

1 Helium or nitrogen precooled gas in through center of transfer tube.

2 Vacuum space of transfer tube.

3 Expanded outer transfer jacket.

4 Ring clamp to limit longitudinal motion.

5 Coolant gas vent.

6 Clamping nut for "O" ring seal.

7 "O" ring.

8 Shoulder with slightly smaller inner diameter to limit travel of other elements.

9 Evacuable space.

10 Copper radiation-shield - mounting collar.

11 Radiation shield.

12 Copper sample block.

13 Sample holder.

14 Window.

Fig. 2 Typical helium flow rates vs. temperatures attained, with and without radiation shield.

3. Optical Phonons and Phase Transition in TiI (K. P. Lowndes and C. H. Perry)

As mentioned earlier pressure dependent studies of the phase transition are in progress and final submission of the material in the form of a more complete report or a scientific publication will await these results.

4. Morphic Effects in Selenium, Tellurium and Other Materials

(K. Anastassakis, B. Hwang and C. H. Perry)

Effects resulting from lowering of the symmetry of a crystal structure due to the presence of an externally applied force are the subject of the present research project. The extension of this work to include a more generalized approach to this type of phenomena, with a complete theoretical analysis and more sophisticated experimental techniques, is being planned. It involves studies on the absorption and Raman scattering by $q \simeq 0$ optical phonons in the presence of external forces such as electric fields or stresses. It turns out that these phenomena can be induced by the external forces even when they are normally forbidden because of symmetry

restrictions. Furthermore, the frequencies of the phonons may exhibit a shift and their degeneracies may be lifted, due to the presence of the forces. From the strength of the induced effects, and the shifts and splittings of the frequencies one can derive numerical values for crystal physical parameters such as induced effective charge, Raman tensor, effective spring constants, etc. These parameters can be calculated theoretically very roughly, and only in a very limited number of simplified symmetries due to the complexity of the problem, thus making their precise experimental determination necessary. Trigonal tellurium offers an excellent type of material to be studied in connection with morphic effects. It turns out that with a suitable choice of unapplied stress, the infrared inactive mode A_1 can become infrared active, while the Raman inactive mode A_2 can become Raman active. The stress can be either uniaxial or shear; special stressing equipments are presently under construction in this department, to allow application of either uniaxial or shear stress.

In the previous report Table 1.1 should have read for tellurium 144 (IR); 143 (Raman); E; E$_{1s}$; σ_{11}, σ_{13}, σ_{31} and 123 (Raman only); A_1; σ_{11}, σ_{33}.

Professor Anastassakis has contacted Professor Burstein and his group at the University of Pennsylvania and it is apparent that they have been undertaking similar Raman studies of Te. As they are about to publish these results it would appear that our interests should now turn to morphic effects, temperature effects and to infrared studies which may have possible electro-optic applications.

5. EuS and EuSe (R. F. Lowndes)

EuS and EuSe are insulating crystals of the NaCl structure. EuS shows a ferromagnetic phase transition at 16°K. EuSe shows an antiferromagnetic phase transition at 8°K. The simplicity of their structure and variability of their magnetic behavior have made these and other europium chalcogenides useful materials for experimental and theoretical studies. We propose to study the dielectric and optical properties of these materials.

6. Other Materials

We would like to start some infrared and Raman studies of proustite (Ag_3AsS_3) and SeS if these could be made available. Studies are also under way on ferroelectric SbSI, antiferroelectric $PbZrO_3$ and $Pb(Zr_{0.95}Ti_{0.05})O_3$ (FE-FE at ~ 63°C, FE-PE at ~ 220°C).

Degrees Granted

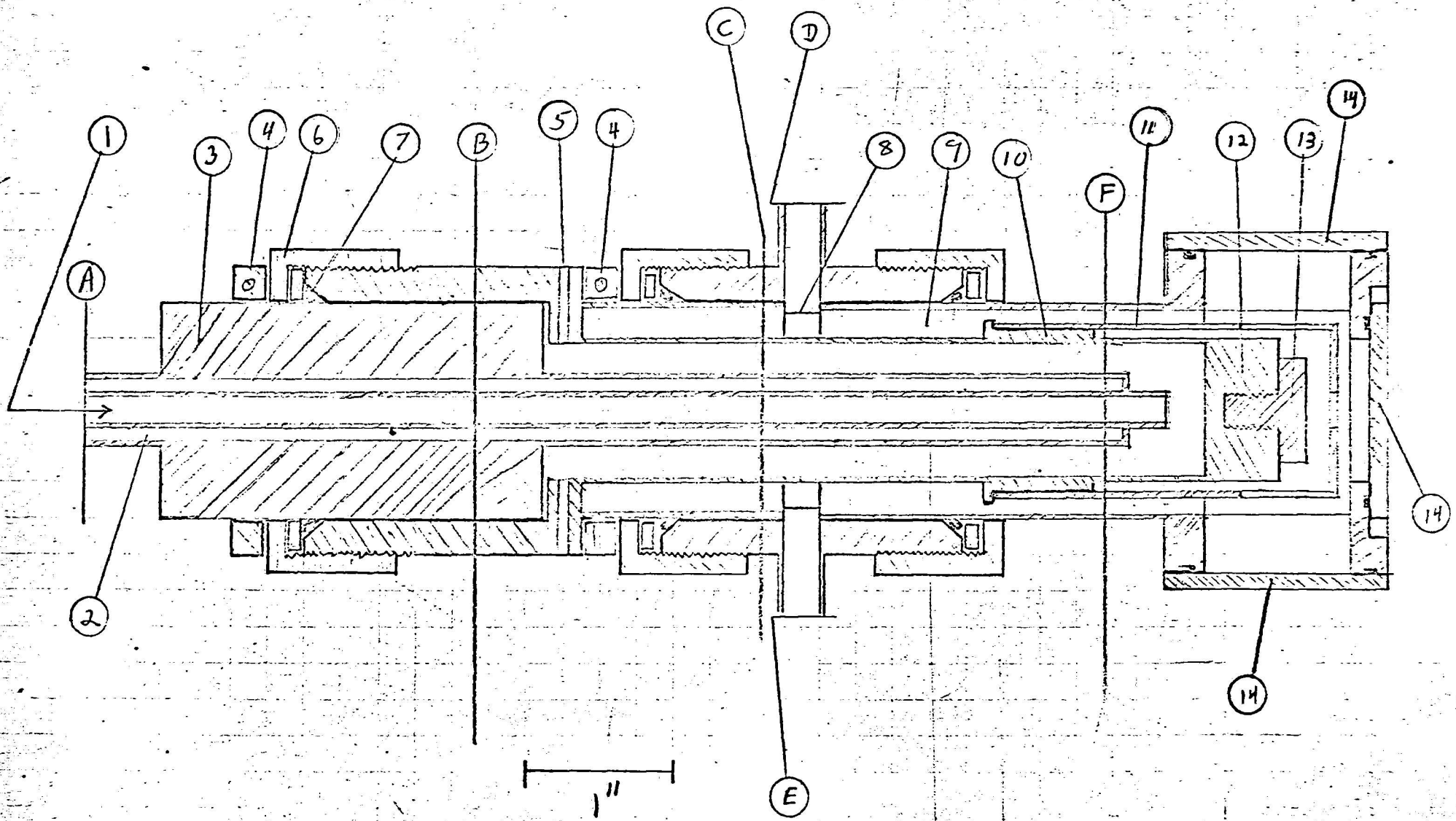
Jeanne M. Fertel, Ph.D., Physics Department, M.I.T., August 1969.

John F. Parrish, Ph.D., Physics Department, M.I.T., October 1969.

Publications Accepted

C. H. Perry and R. F. Lowndes, "Optical Phonons and Phase Transitions in the Ammonium Halides" (J. Chem. Phys.).

H. E. Torneberg and C. H. Perry, "A Variable Temperature (8-400°K) Gas Transfer Cell for Solid State Spectroscopy" (Applied Optics).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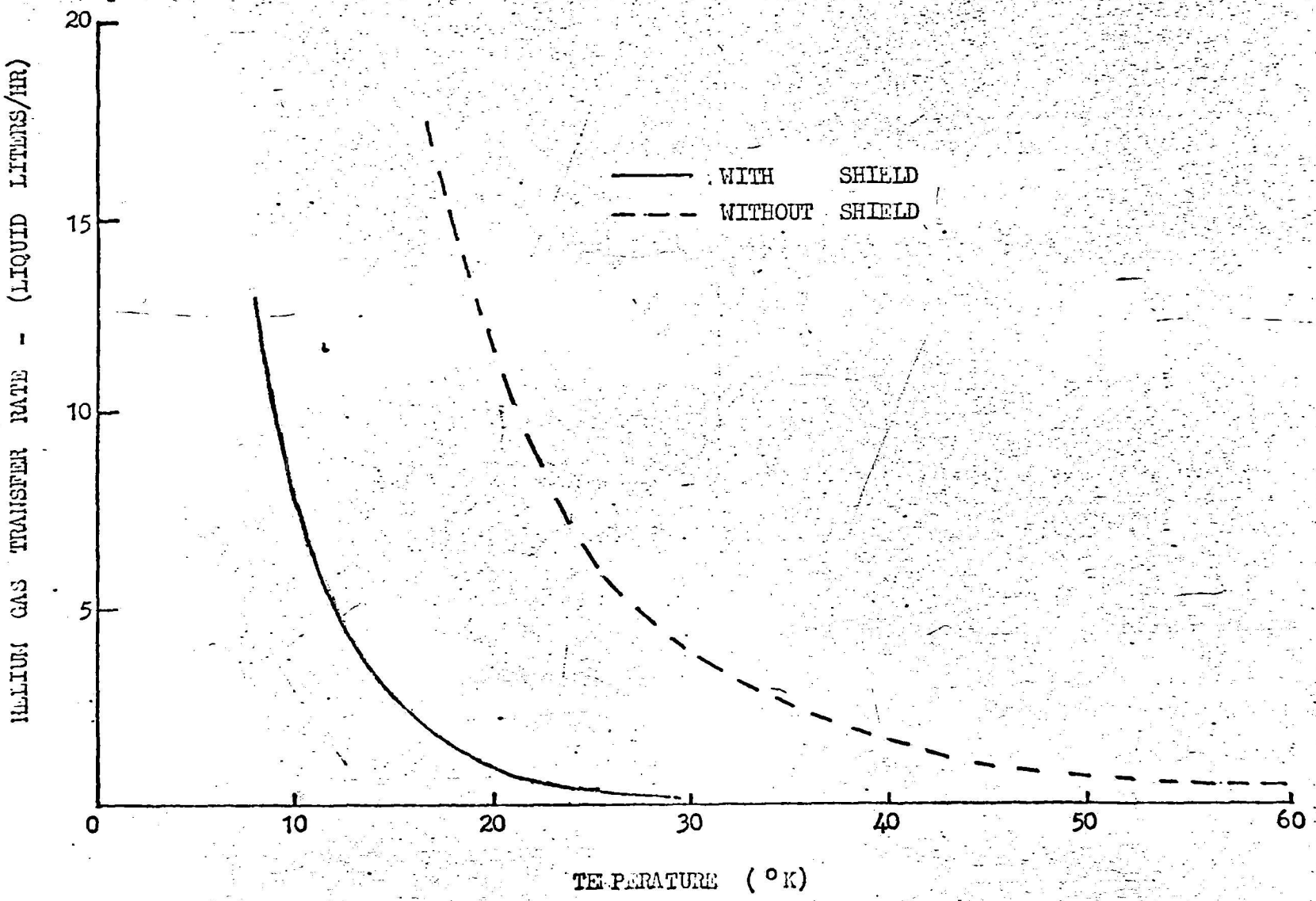
HELIUM GAS TRANSFER RATE - (LIQUID LITERS/HR)
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40
50
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TEMPERATURE (°K)
WITH SHIELD
WITHOUT SHIELD