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THE DEVELOPMENT OF FERROMAGNETIC SPINELS FOR OPTICAL ISOLATION AT 10.6 μm

Progress Report

for Period August 1, 1976 - April 30, 1977

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DISCLAIMER

ABSTRACT

During the period August 1, 1976 to April 30, 1977 small single crystals of $CdCr_2S_4$ and $CoCr_2S_4$ were grown. The absorption coefficient, α, of $CdCr_2S_4$ crystals was measured at 10.6 μm and correlated with growth parameters. The best result to date was $\alpha = 15.5\ cm^{-1}$. An analysis of the intrinsic absorption of $CdCr_2S_4$ at 10.6 μm was made indicating a lower limit to α of $10^{-4} cm^{-1}$. Measurements of α vs. λ in hot pressed disks of $CdCr_2S_4$ reveal that the most probable impurity affecting α at 10.6 μm is $SO_4^{=}$. Equipment and facilities for preparing materials in an oxygen free environment are being constructed. A TEM_{oo} pulsed CO_2 laser for damage tests has been purchased and is being set up.

TECHNICAL PROGRESS REPORT

The Development of Ferromagnetic Spinels for Optical Isolation at 10.6 μm

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I. Progress to Date

A. Scope of Work

The principal investigator, Kenneth Teegarden, was on sick leave for the months of September and October 1976. This resulted in a reduction of effort on this contract for those two months and some delay in ordering major items of equipment needed for later parts of the work. Also, delay in hiring a research associate, who will represent a major fraction of the manpower involved in the project, was experienced. In spite of this, significant progress has been made in preparing and evaluating $CdCr_2S_4$ and $CoCr_2S_4$ for use as Faraday isolators for 10.6 μm radiation. Nothing has occurred which causes us to deviate from the approaches presented in the original proposal. The most critical part of the effort, namely, the reduction of optical absorption at 10.6 μm, has or will be completed by the end of the contract period.

B. Materials Preparation

Small single crystals (< 2mm. diameter) of both $CdCr_2S_4$ and $CoCr_2S_4$ have been prepared using a liquid phase technique similar to that described by Schick and Von Neida (1). The advantage of this approach, compared to others which result in a fine powder (2), is twofold. It is possible to grow the crystals in vacuum or an atmosphere which excludes oxygen, and

produce materials which can be characterized before hot pressing. Thus, the intrinsic optical properties can be determined and the effect of hot pressing evaluated. The failure to recognize the need for these two steps in previous work has resulted in material with unreproducible absorption at 10.6 μm.

A significant improvement over the original technique of Schick and Von Neida has been achieved in our work. We have been able to successfully grow crystals using Cd foil as a getter material rather than Pt foil. This is quite important as it markedly reduces the cost of materials production. In our pilot studies, the absolute amount of money saved is not great. However, in future applications of the ferromagnetic spinels such a saving would be quite large. It should also be mentioned that we believe this is the first time $CoCr_2S_4$ has been prepared by the liquid phase technique. Our success encourages us to believe that most, if not all, of the spinels can be prepared this way, and opens the way to developing new magnetic, semiconductors for room temperature operation.

The various modifications in our procedure for $CdCr_2S_4$ and the size of the resulting crystals are listed in Table I. It appears that larger crystals occur when a Cd foil getter is used.

Procedures for hot pressing or forging $CdCr_2S_4$ are currently being worked out. It is important to forge at as low a temperature as possible to avoid decomposition and consequent deterioration of optical properties. To aid in attaining a clean environment for forging, a 7.5 KW R.F. induction heater has been purchased and will be set up during the last three months of this

contract. This new equipment was specified in the scope of the contract.

C. Optical Characterization

Perhaps the most important step in the development of $CdCr_2S_4$ and $CoCr_2S_4$ for isolator applications is the measurement of absorption coefficient, α, at 10.6 μm and the correlation of α with methods used to prepare crystals and hot-pressed disks. Single crystals about 2 mm. on a side were polished to various thicknesses and mounted over 20.5 mm. diameter aperture. The transmission of these crystals was measured using a 1 watt CO_2 laser operating at 10.6 μm. Since the reflection coefficient of $CdCr_2S_4$ is known (3), α can be calculated from the measured transmission. Although this method is time-consuming and tedious, it is needed to establish the intrinsic value of α, and to determine the success of various preparational methods in bringing α down to this intrinsic value. The value of α at 10.6 μm resulting from various modifications of the liquid phase technique employed in this work is shown in Table II. The best value of α so far achieved was 15.6 cm^{-1}. It is felt that this value exceeds the intrinsic limit by several orders of magnitude, and is determined by impurity absorption. The most likely impurities are oxygen containing complexes, as shown in Section C2.

An imperical investigation, based on recent theories of the reststrahl edge in laser window materials (4), was undertaken to estimate the intrinsic value of α at 10.6 μm in both $CdCr_2S_4$ and $CoCr_2S_4$. In Fig. 1 is plotted the natural logarithm of α vs. photon energy for $CdCr_2S_4$ in the reststrahl tail. Values of α large enough to exclude extrinsic effects lie on a straight

line in this plot. Such a dependence of reststrahl absorption on photon energy is expected according to current theories. Of interest to us is the extrapolated value of α at 10.6 μm. This turns out to be 10^{-9} cm^{-1}. If the effect of multiphonon processes is taken into account, following procedures developed for the alkali halides and other laser window materials (4), a value of α 10^{-5} or 10^{-4} cm^{-1} is projected. Data for $CoCr_2S_4$ is not as free from extrinsic effects, but a similar extrapolation yields a value of α = .1 cm^{-1}. In either case it is apparent that in our crystalline material, α is still dominated by extrinsic effects.

In order to establish the absorption mechanism determining α at 10.6 μm, measurements of α as a function of photon energy were made. Because of the size of the single crystals, these measurements could only be made on polycrystalline samples produced by hot pressing. As an example of the results of this work, the transmission spectra of two samples of hot pressed $CdCr_2S_4$, prepared from powders, are shown in Figs. 2 and 3. In Fig. 2, the transmission of a high quality pressed disk is given. This data is not corrected for reflection losses, so no absolute value of α can be derived from it. However, the α of this sample was measured to be 2.9 cm^{-1} at 10.6 μm. It is, therefore, quite transparent in most of the region covered in the figure. The only extrinsic feature of this spectrum is the absorption band or bands near 14 μm, on the shortwave length tail of the reststrahl band which causes strong absorption above 15 μm. In Fig. 3 appears the transmission of a sample of hot-pressed $CdCr_2S_4$, prepared in the same way as the sample

of Fig. 2. The transmission, however, is much lower at 10.6 μm. This sample shows evidence of scattering losses and an absorption band at ~ 9 μm, as well as the structure at 14 μm. This illustrates the situation to date: the best materials always show absorption bands near 14 μm, the poorest also show absorption at 9 μm. The question as to the origin of these extrinsic absorption bands and their influence on α at 10.6 μm is central to the optimization of $CdCr_2S_4$ for isolator applications at 10.6 μm. It has been suggested that the 14 μm complex is due to Cr_2O_3 (4). The origin of the 9 μm band has not been previously determined.

We have studied the effect of doping hot-pressed $CdCr_2S_4$ with .1 and .01% of Cr_2O_3. Neither absorption at 9 μm or 14 μm was enhanced by this addition. Its only effect was to introduce considerable scattering and a slight broadening of the reststrahl tail, probably due to Cr_2O_3 existing as a second phase in the material. Absorption at 10.6 μm was not influenced by these massive additions of Cr_2O_3. In fact, the absorption coefficient of the doped material at 10.6 μm was among the lowest encountered in hot-pressed samples of $CdCr_2S_4$. On the other hand we have found that that the complex $SO_4^{=}$ shows strong absorption at 9 μm, with weaker bands very near 10.6 μm. An example of the transmission of $CdSO_4$ in KBr is shown in Fig. 4. We feel that these results show oxygen to be of major importance in determining the extrinsic absorption at 10.6 μm in $CdCr_2S_4$. However, the complex $SO_4^{=}$, not Cr_2O_3 as previously thought, is the specific absorbing impurity.

D. Laser Induced Damage

Preliminary damage studies indicated a threshold in excess of .5 v/cm^2 for 2 1 nsec pulse. These measurements, however, used a multimode CO_2 laser and did not include the effect of possible mode=locked spikes in the laser output. Following the scope of this contract, a TEM_{oo} mode CO_2 laser has been purchased specifically for damage tests on $CdCr_2S_4$ and other materials produced in the course of the work. This laser is presently being set up and will be in operation during the last three months of this contract. A photon drag detector which will allow monitoring of the time evolution of the laser pulse is being purchased, along with an appropriate oscilloscope.

E. Personnel

In addition to the personnel currently working on the contract (K. Teegarden, and graduate students Robert Freese and John Stulak), Dr. Achim Bubenzer will begin an appointment as research associate on May 15, 1977. Dr. Bubenzer has a background in crystallography and optical materials which will greatly aid the progress of the work. He was selected from several candidates for the position.

II. Projections for the Laser Quarter

During the last three months of this contract, emphasis will be placed on producing hot forged blanks of $CdCr_2S_4$ with $\alpha = .1$ cm^{-1} or less. We feel that this will be accomplished by monitoring the concentration of SO_4 complex in our starting materials and excluding oxygen from all stages of the fabrication process. Facilities for handling materials in an inert atmosphere

have already been constructed. The change from resistance heating to induction heating in our forging process will also aid in maintaining a controlled atmosphere.

Measurements of α in $CdCr_2S_4$ at 77^o K, as well as at room temperature, will form an important part of the work to be accomplished during the next three months. Preliminary results indicate a decrease in α of as much as a factor of 10 at 77^o K. Since $CdCr_2S_4$ must be cooled below 80^o K for isolator operation, advantage can be taken of this decrease in practice. Also, the temperature dependence of α can provide information about the mechanisms responsible for absorption at 10.6 μm.

Damage tests on forged and single crystal samples may be initiated during the last quarter, depending on any unforeseen difficulties encountered in setting up the TEM_{oo} mode laser and associated equipment.

If acceptable values of α are achieved in $CdCr_2S_4$ before the end of the contract period, measurements of specific Faraday rotation, passive extinction ratio, and forward to back extinction ratio may be initiated. Our best estimate, however, is that these measurements will not be completed before the end of the contract period.

III. Personnel

The principal investigator devoted 30% of his time to this project during the reporting period, except for the months of September and October, when he was on sick leave. During the last three months of this contract, he will devote 30% of his time during May, and 100% of his time during the months of June and July.

Also, Dr. Achim Bubenzer has accepted an appointment as Research Associate starting May 15, 1977. He will devote 100% of his time from then until July 31, 1977.

References

1. A.R. Von Neida and L.K, Shick; J. Appl. Phys. 40 1013 (1969).

2. D. Pearlman, E. Carnall, Jr., and T.W. Martin; J. Sol. State Chem. 7 138 (1973).

3. F. Moser, R.K. Ahrenkiel, E. Carnall, T. Coburn, S.L. Lyu, T.H. Lee, T. Martin and D. Pearlman; J. Appl. Phys. 42 1449 (1971).

4. T.F. Deutsch; J. Phys. Chem. Solids 34 2091 (1973).

TABLE I

The Growth of $CdCr_2S_4$ Crystals

Trial	Conditions	Observations
1	Method used by T. Cheng & Shick & Von Neida	Small (< .3 mm/side) crystals observed, quartz tube cracked
2	Repeat #1	Explosion
3	Trial #1 with reduced quantities T=850°C for 3 days. Mole ratio 2.21/1/.45 (CdS, $CoCl_3$, Cd foil)	Large (1.1 mm/side max.) crystals produced
4	Change temperature to 800°C	Crystals as large as in #3 produced
5	Tilt furnace at 20° angle 50° Temp. gradient across quartz tube	Largest (1.5 mm/side) "Imperfect" crystal
6	Platinum getter instead of Cd	Tiny (< .3mm/side) but "Perfect" crystals
7	8 hour linear cool down of furnace (normally 4 hour exponential)	Large (1mm/side) but "Perfect" crystals
8	Change mole ratio to 1.5/1/.45 keeping amount of $CrCl_3$ consistent	Smaller crystals than trial 3. Also smaller yield
9	Mole ratio to 2.5/1/.45	Highest yield of large (mm) crystals
10	Combination temp. gradient and inclination; T=800°C Cd foil getter, 8 hour cool down, 2.5/1/.45 mole ratio	Nothing special, yield and sizes near that of trial 3.

TABLE II

$CdCr_2S_4$ Room Temperature Absorption Coefficient Results

Trial	Crystal Growing Method	Range of Polished Crystal Thickness (μm)	Range of absorption Coefficients (cm^{-1})
3	Schick & VonNeida method temp.=850°C, mole ratio 2.2/1/ .788 (CdS, $CrCl_3$, Cd) exponential cool down	209 - 536	45.0 - 102
4	Trial 3 with temp.=800°C	285	15.6
5	Trial 3 with furnace tilted at 20° angle, 50°C gradient across tube	382 - 534	41 - 72
7	Trial 3 with linear cooling rate	380 - 465	50 - 76
8	Trial 3 with mole ratio 1.5/1.0/ .788 (CdS,$CrCl_3$Cd) keeping amount of $CrCl_3$ constant	270 - 272	33 - 75.0
9	Trial 8 with mole ratio 2.5/1.0/ .788 (CdS, $CrCl_3$, Cd)	412 - 455	19.8 - 43
10	Shick & Von Neida method only temp.=800°C, mole ratio 2.5/1/ .788, linear cooldown, 20° angle tilt, 50°C gradient	283 - 301	63 - 101

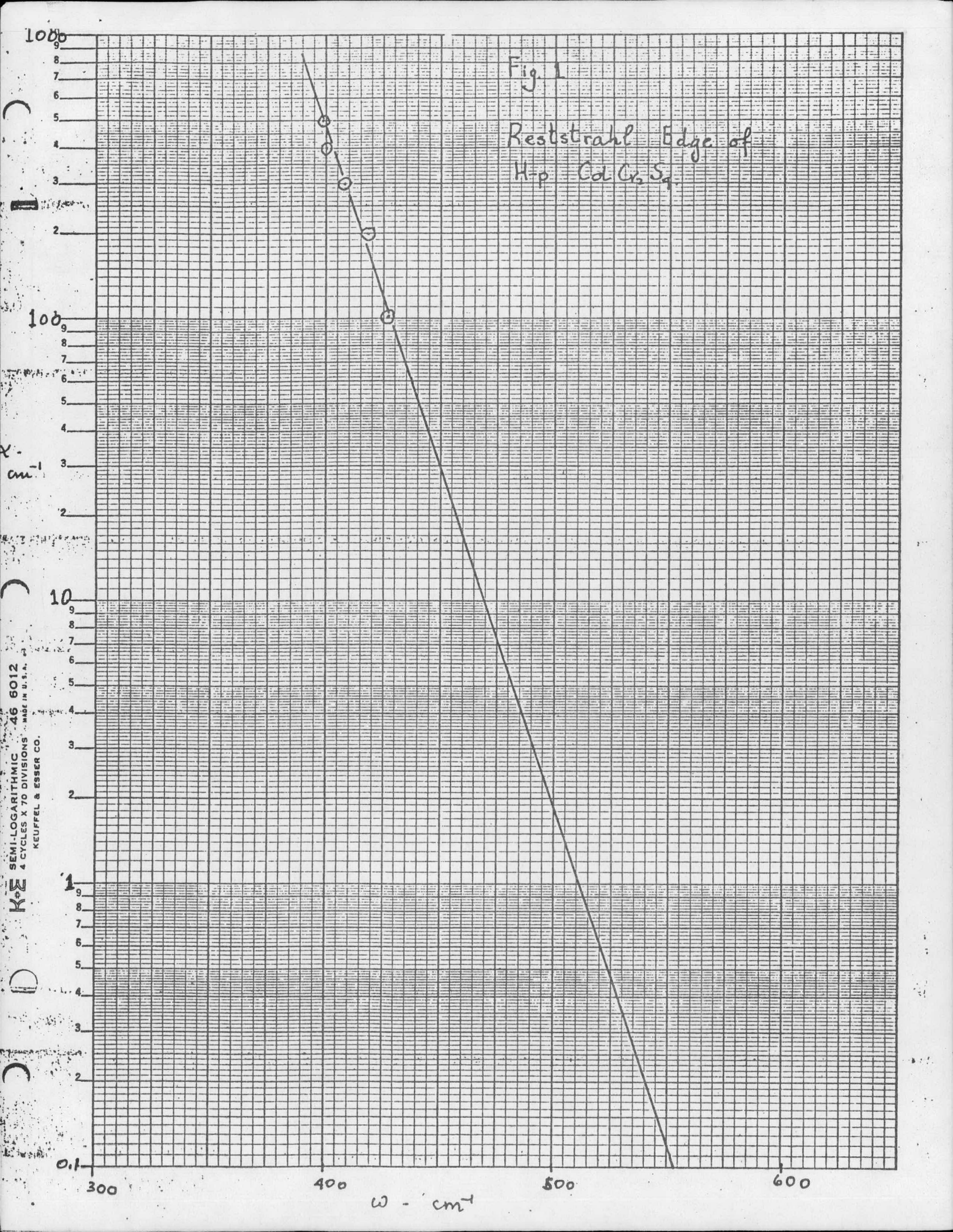
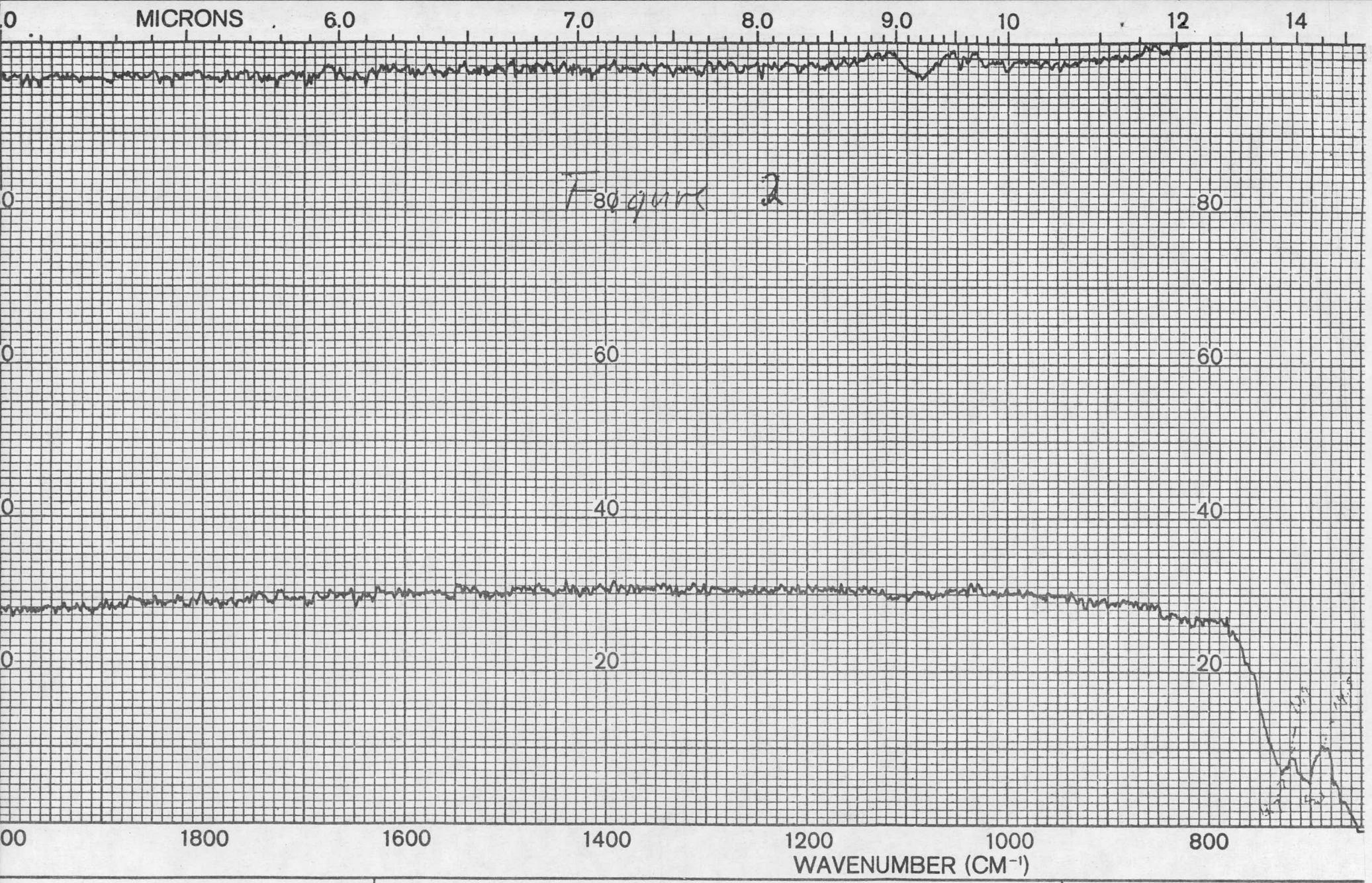


Fig. 1
Reststrahl Edge of
H-p Cd $Cr_2 S_4$
1000
100
10
1
0.1
χ - cm^{-1}
300
400
500
600
ω - cm^{-1}
K+E SEMI-LOGARITHMIC 46 6012
4 CYCLES X 70 DIVISIONS MADE IN U.S.A.
KEUFFEL & ESSER CO.



REMARKS Transmission of hot pressed $CdCr_2S_4$ at room temperature. The absorption constant α was measured to be 2.90 at 10.6 μm, using a CO_2 laser.

SCAN SPEED

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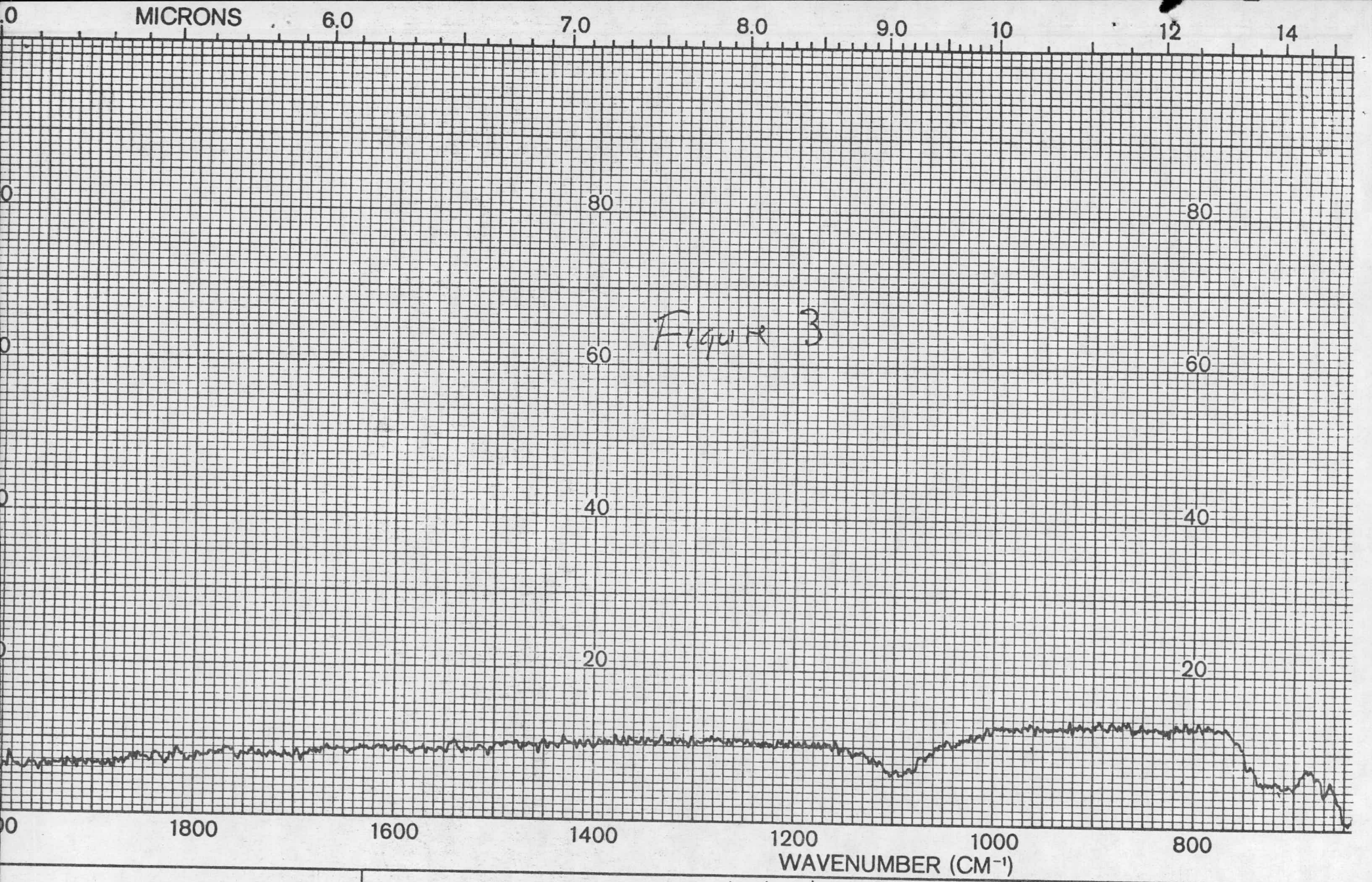

Figure 3

REMARKS Transmission of hot pressed $CdCr_2S_4$ showing absorption at 9 μm due to $SO_4^=$, and scattering.

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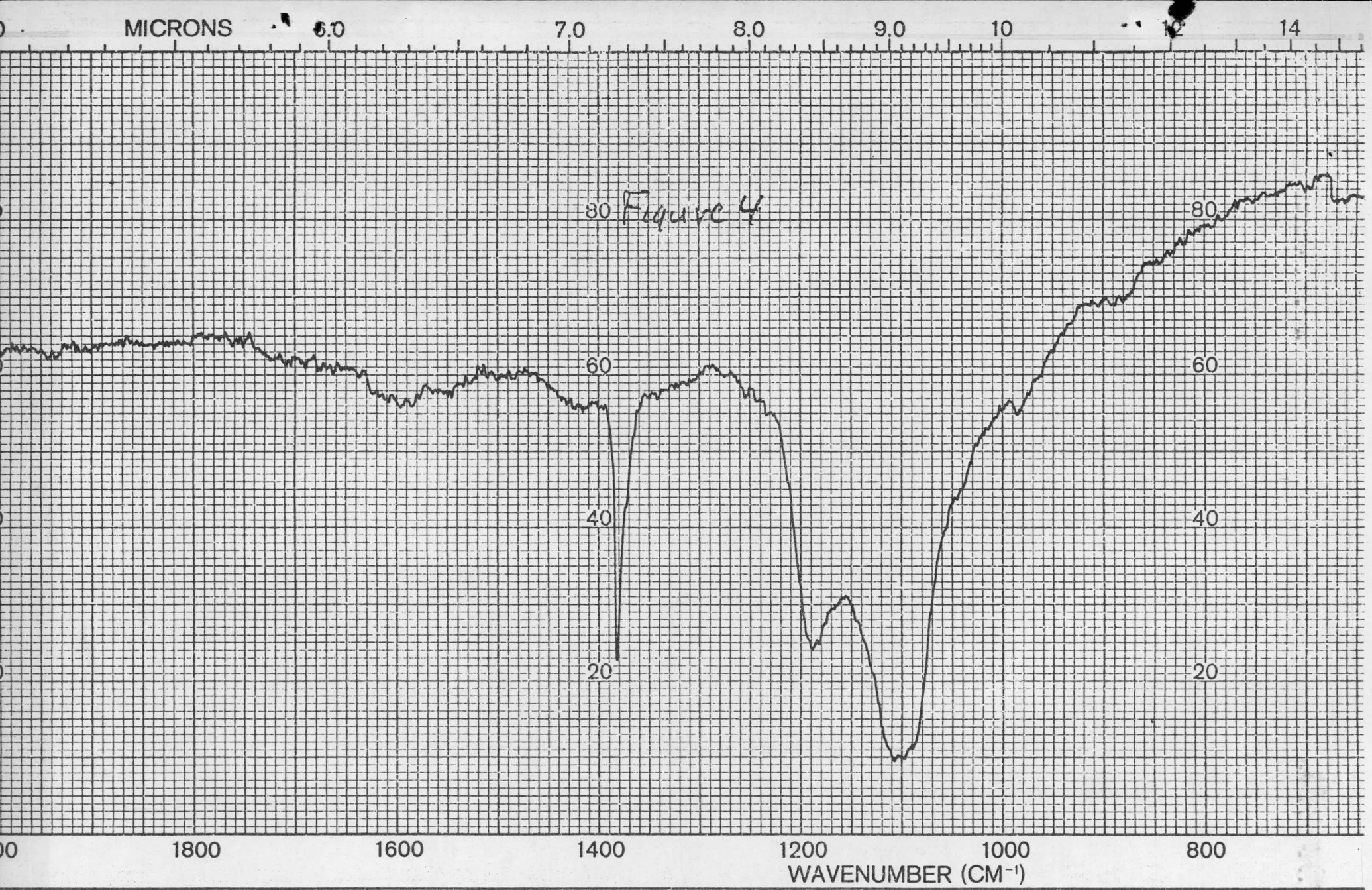

REMARKS Absorption spectrum of $CdSO_4$ in a KBr Pellet. Note Characteristic $SO_4^{=}$ absorption at 9 μm.

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