regions and also with the chemical analysis of the landing site of Surveyor 5 (*7*).

We may inquire why the bands in the lunar color profiles reported here have not been seen before. Although a single shallow band has been reported (*4, 5, 8*), the other bandlike depressions seem to become visible only when very small regions on the moon, each having a certain degree of mineralogical integrity, are observed. The other observers mentioned above have measured the reflectivity of areas somewhat larger than those investigated here.

D. P. CRUIKSHANK
Lunar and Planetary Laboratory, University of Arizona, Tucson 85721

References and Notes

1. G. P. Kuiper, R. B. Goranson, A. B. Binder, H. L. Johnson, *Commun. Lunar Planet. Lab.* **1**, 119 (1962).
2. D. P. Cruikshank, thesis, University of Arizona (1968).
3. A. B. Binder and D. P. Cruikshank, *Commun. Lunar Planet. Lab.* **5**, 111 (1966).
4. R. G. Tull, *Icarus* **5**, 505 (1966).
5. V. I. Moroz, *Sov. Astron. AJ Engl. Transl.* **9**, 999 (1966).
6. J. B. Adams, *Science* **159**, 1453 (1968).
7. A. L. Turkevich, E. J. Franzgrote, J. H. Patterson, *Jet Propulsion Lab. Tech. Rep. 32-1246* (1967), p. 119.
8. R. B. Wattson and R. E. Danielson, *Astrophys. J.* **142**, 16 (1965).
9. Dr. A. B. Binder and A. B. Thomson assisted with the observations and reductions, respectively. I thank Drs. S. R. Titley and G. P. Kuiper for valuable criticism. Supported by NASA contract NsG 61-161 with the Lunar and Planetary Laboratory.

29 January 1969; revised 30 July 1969 ■

Sulfur Melting and Polymorphism under Pressure: Outlines of Fields for 12 Crystalline Phases

Abstract. *The polymorphism of sulfur has been investigated by static and dynamic methods up to 500°C at 35 kilobars and up to 350°C at 100 kilobars. The melting curve of sulfur to 31 kilobars and phase boundaries of the so-called "4.04-angstrom phase" have been determined. Evidence has been obtained for phase fields of nine new high-pressure forms of sulfur.*

Baak (*1*) has reported a new "cubic" form of sulfur at pressures greater than 30 kb below the liquidus and another phase with a single diffraction maximum at 4.04 Å. He theorized that the 4.04-Å peak corresponded to the (220) reflection (4.06 Å) of rhombic sulfur and that the crystallization from the liquid state under high pressure was oriented along this plane.

Using a piston-cylinder apparatus with a solid pressure-transfer medium, Geller (*2*) obtained three crystalline phases (I, II, III) by first melting sulfur under pressure and then inducing crystallization by lowering the temperature. None of these phases matches the cubic phase reported by Baak, although the strongest x-ray peak of phase II occurs at 4.03 Å, thus almost coinciding with the single reflection of Baak's second phase. Sclar *et al.* (*3*) reported a quenched high-pressure phase which they designated as the "4.04-Å phase," obtained by the use of a belt apparatus and temperature quenching under pressure. The *d*-spacing data of these workers for this phase are practically identical with those of Geller's phase II, and both Sclar *et al.* and Geller point out the similarity of the diffraction patterns to that of the fibrous or ψ form of sulfur. Geller indexed phase II on an orthorhombic cell and narrowed the space group assignment to three possibilities. Sclar *et al.* reported data on the pressure-temperature range of formation of the liquid and the high-pressure form. Paukov *et al.* (*4*) observed a sharp decrease in the compressibility of sulfur at 22.5 kb and room temperature; this suggests the possibility of transition to a high-pressure polymorph. These workers also reported a fusion curve out to about 37 kb which showed a maximum at 310°C and 16 kb and a minimum at 290°C and 19 kb.

The results of Geller (*2*), Sclar *et al.* (*3*), and Paukov *et al.* (*4*) and the fusion curves of Susse *et al.* (*5*) and Ward and Deaton (*6*) support the qualified suggestion (*3*) that the 4.04-Å phase exists in equilibrium with the liquid between 30 and 60 kb. A field for this phase probably will have at least two triple points below 30 kb. However, on the basis of Baak's results, Geller's report of quenched phases (I, III), and other fusion curves (*7*), one may only conclude that thus far (i) one high-pressure crystalline form of S has been found (*1–3*) (Baak not recognizing it as such); (ii) there have been isolated reports of three other new crystalline phases; and (iii) the placement of any stability field is impossible.

The techniques utilized here included optical and x-ray studies of the thermally quenched product, volumetric and electrical measurements *in situ* at high pressure and temperature, high-pressure differential thermal analysis (DTA), and x-ray and optical analysis at high pressure and temperature. In the quench and electrical runs, pressure and temperature were applied by the opposed-anvil system (*8*) whereas experiments designed to determine volume discontinuities were based on a simple externally heated, piston-cylinder type of apparatus consisting of Bridgman unsupported area–seal steel pistons or tungsten carbide pistons (1.27 cm in diameter) and a closely fitted cylinder of René 41. Gaskets were made of soft annealed nickel disks or rings 0.05 cm thick. Optical studies at high pressure and temperature were made by means of an opposed–diamond anvil system. For DTA experiments argon under pressure was applied to both sample and reference, hermetically sealed in platinum tubes inside a pressure vessel with an inner diameter of 1.27 cm. In all cases temperatures were measured with Chromel-Alumel or Platinel II thermocouples outside the pressure field (except in the DTA experiments). Temperatures and pressures are believed to be accurate to ± 2°C and ± 5 to 10 percent, respectively. The techniques used avoid or minimize any tendency for the establishment of pressure gradients in the sample. Flowers of sulfur (sublimed) (Fisher Scientific Company, 99.9 percent purity) and high-purity sulfur (American Smelting and Refining Company, 99.999 percent purity) were used as starting materials. The latter was stored in a vacuum desiccator and was used for 75 percent of all runs and for each of the critical runs.

Figure 1 summarizes our interpretation of the results from over 700 runs made with various types of apparatus. The major features of the liquidus are based on 70 quench runs in the opposed-anvil apparatus in which temperature and load pressure were continuously monitored by an observer. Sets of runs were repeated three times in the region of the liquidus that displays the slight "maximum" about 17 kb. A cusp (intersection of smooth arcs) indicates a triple point formed by the intersection of a solid-solid boundary with the liquidus. Results obtained in the solid-phase region showed that the phase boundaries between phases IV and VI, VI and VIII, and VIII and XII are related to the three cusps shown in Fig. 1. Paukov *et al.* reported a maximum and a cusp at about 16 kb and 310°C and at 19 kb and 290°C, respectively, whereas Susse *et al.* located these features at 15 kb and 300°C and at 19 kb and 290°C, respectively. Our results place them at 17 kb and 348°C and at 18 kb and 345°C, respectively.

Our work with the opposed-anvil system indicated that, although we had many indications of several phase changes below the liquidus, the only high-pressure phase that could be quenched to room conditions by the usual air-blast cooling technique was phase XII (the 4.04-Å phase of Sclar *et al.*). Samples quenched from all other accessible pressure-temperature regions invariably crystallized as rhombic sulfur. Attempts to cause phase XII to revert to other solid phases at pressures and temperatures other than those within field XII were unsuccessful despite the use of runs of long duration. Furthermore, this phase persisted at room conditions indefinitely (over 2 years). Sclar *et al.* reported that this phase inverted slowly at room conditions, to the extent of 60 percent in 10 days.

In the absence of clearly quenchable phases for which good x-ray diffraction data could be obtained, it was difficult to believe in the existence of so many new polymorphs of sulfur (Fig. 1). However, by using a technique in which the products of the opposed-anvil runs were quenched under pressure to dry-ice conditions and were then x-rayed immediately at about −20°C (*9*), we obtained diffraction patterns that were characteristic of the pressure-temperature fields from which the quenching was done. Most of the products contained a considerable proportion of rhombic sulfur, but in some of them definite concentrations of other phases were present. The x-ray diffraction data from this series of runs are summarized in Table 1. The new diffraction lines, obtained from the products on quenching from some of the phase fields, may be those of the respective phases or of metastable phases derived from them by rapid transitions during the quenching process; at this time a clear assignment is not possible.

The isothermal experiments, conducted in the piston-cylinder apparatus, disclosed volume discontinuities that were attributed to transitions from phase I to phase III, III to V, V to VII, VII to IX, and VI to VIII. The most pronounced discontinuity occurred during the transition from phase VII to phase IX; this may correspond to the discontinuity at 22.5 kb and room temperature for which Paukov *et al.* reported a sharp decrease in compressibility. Volumetric runs under isobaric conditions provided additional indications of the phase boundaries stretching out from 120°C to 130°C and 2 kb to about 26 kb and for those of the transitions from phase VI to phase VIII and that from phase VII to phase IX (Fig. 1).

Sulfur remains an insulator over the region of the phase diagram under study. However, when fine nickel powder was mixed with sulfur (1 : 1 by volume), discontinuities in electrical resistance with pressure were observed that are apparently related to phase changes of sulfur. For example, a discontinuity, detected by the volumetric method at about 12 kb and room temperature (III-V boundary), was consistently observed at about the same pressure with the electrical-resistance setup and the nickel-sulfur mixture. Similarly, there was a fair amount of

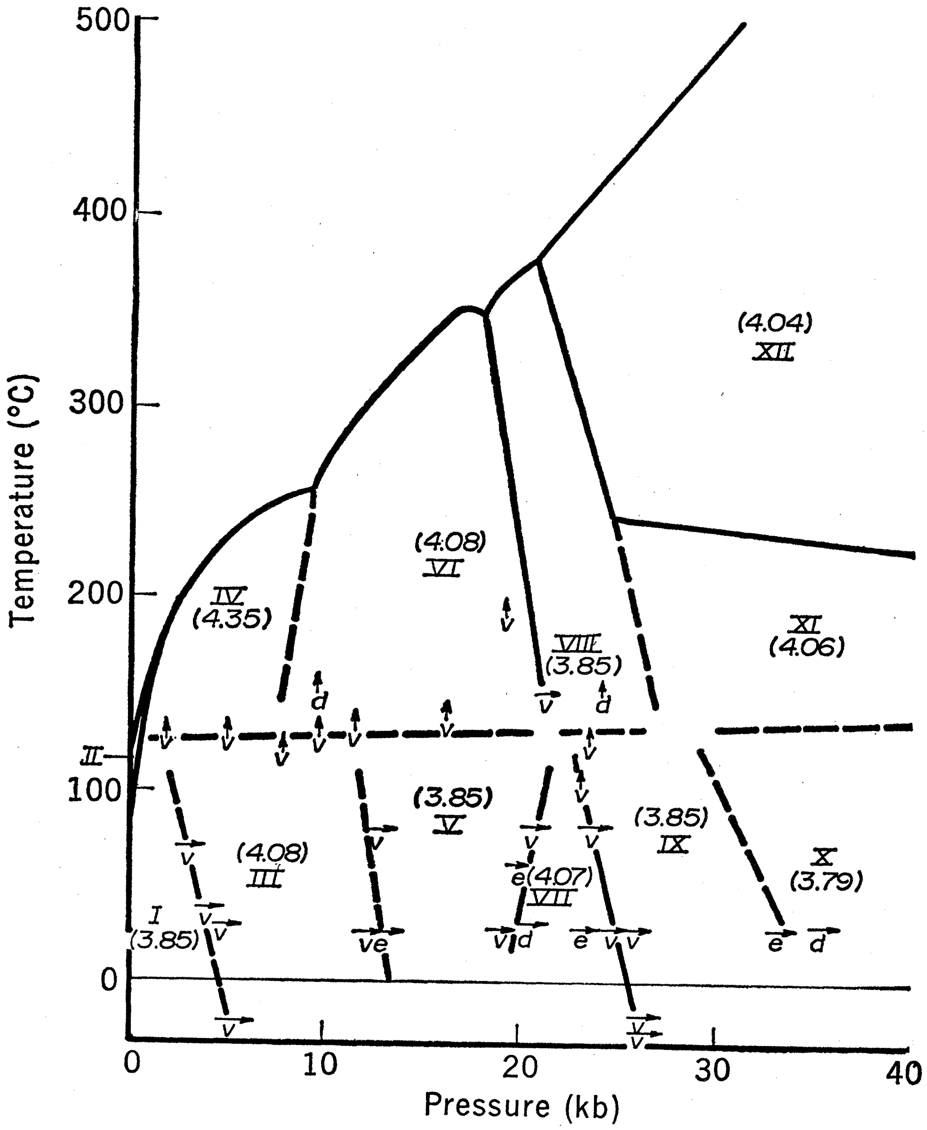

Fig. 1. Summary of data on sulfur to 40 kb and 500°C (below 350°C the diagram may be extended out to 100 kb). Symbols refer to transitions determined with the following techniques and apparatus: *v*, volumetric (simple piston-cylinder); *d*, optical (diamond-anvil system); *e*, electrical resistance (Ni-S mixtures). Dashed lines indicate boundaries for which confirmation is not complete. The number in parentheses in each field is the characteristic *d*-spacing of the major diffraction line, obtained from products of runs quenched from the specified field to low temperatures. Only rhombic sulfur was present in the product from fields marked 3.85; other values signify that another phase was present (see Table 1).

coincidence between volumetric and resistance discontinuities for the transitions from phase V to phase VII and that from phase VII to phase IX. Therefore, a resistance discontinuity near 33 kb at room temperature was interpreted as some evidence for the transition from phase IX to phase X.

The electrical-resistance data were quite reproducible (± 1.5 kb), but the reasons for such behavior are not known. Examination of the x-ray diffraction patterns of the product indicated that there was no noticeable reaction of sulfur with nickel. Furthermore, the effect of pressure on the resistance of pure nickel in the same apparatus showed no discontinuities or discontinuous slope changes. Finally, duplication of the results, after the substitution of platinum for nickel, furnished some confirmation that the effect was initiated by the behavior of the sulfur. Details of the resistance experiments are given by Vezzoli (*10*).

In addition to the definite resistance break at 20 kb, details of resistance changes with pressure provided another indication of discontinuity. The difference between initial and steady-state readings of the electrical resistance of the nickel-sulfur mixture, with each increment of pressure, consistently showed a change in sign at the transition from phase V to phase VII. A similar phenomenon was observed in the study of germanium (*9*).

A diamond-anvil system (*11*) was used to optically observe phase transitions in sulfur with pressure. The pressures attained in the unit were based on calibration runs in which color changes were observed at the 3-kb and 4-kb transitions in AgI and the 19-kb transition in KCl. At room temperature, with white light, color changes of the sample, which we attributed to the transitions from phase V to phase VII, phase VII to phase IX, and phase IX to phase X, were observed as the pressure was increased to about 60 kb. The sequence of color change was yellow to reddish-orange to a very deep red to black. The pressures at which these changes occurred are shown in Fig. 1. The same technique was used to observe changes as the temperature increased and helped to determine the V-VI, IX-VIII, and X-XI boundaries, the change for the X-XI boundary being observed at about 56 kb and 140°C.

The use of the high-pressure x-ray unit showed that, at a pressure of 8 to 9 kb, the major diffraction lines of orthorhombic sulfur disappeared when the temperature was raised above 120°C. However, no consistent x-ray data were obtained that could be used to characterize new phases stable above 120°C.

The x-ray diffraction patterns (Table 1) have some relation to the fields from which the samples were thermally quenched to low temperatures. If we consider the phase sequence I, III, V, VII, IX, and X, the products from fields I, V, and IX produce only the rhombic sulfur pattern, whereas the alternate phases, III, VII, and X, give new lines in addition. Furthermore, the contiguous pairs of phases III-IV, V-VI, VII-VIII, and X-XI (each pair of which was quenched essentially along an isobar) show sharp differences in the diffraction patterns of the products quenched to and x-rayed at dry-ice conditions. In our interpretation, phases V, VIII, and IX must revert completely to the rhombic form despite the rapid quenching; the volumetric, electrical-resistance, and diamond-anvil optical data furnish supportive evidence for the existence of these phases.

Table 1. The *d*-spacings (x-ray diffraction powder patterns) of products of runs thermally quenched from various pressure-temperature fields. The data are given for products quenched from the central portions of the indicated phase fields. The *d*-spacings were measured at about −20°C for all except phases II and XII. The lines for the monoclinic phase are those reported by Pinkus *et al.* (*15*); those we obtained for phase XII are practically identical with the values of Geller (*2*) and Sclar *et al.* (*3*). Except for phases II and XII, all the products contained rhombic sulfur; phase IV apparently contained only a very small amount of rhombic sulfur. The boundaries of phase II, determined by DTA measurements under pressure, agree approximately with those of Tammann (*12*). Intensities: s, strong; vs, very strong; ms, moderately strong; m, moderate; mw, moderately weak.

Phase	Quenched from		*d*-Spacings of new lines and intensities (Å)
	Pressure (kb)	Temperature (°C)	
I	1.5	55	None
II (*15*)	Monoclinic		3.29(s), 6.65(mw), 3.74(mw)
III	7.5	75	4.08(s)
IV	5.0	175	4.35(m), 3.16(m)
V	17.5	100	None
VI	16.0	235	4.08(s), 3.20(m), 3.42(m)
VII	21.5	70	4.07(ms)
VIII	26.0	140	None
IX	27.5	48	None
X	39	25	3.79(vs), 4.09(vs), 3.56(m)
XI	39	156	4.06(s), 4.33(m)
XII (*2, 3*)	40	350	4.04(s), 3.22(m), 2.90(mw)

Thus it appears that only the transformations from phase VIII to phase XII and from phase XI to phase XII are reconstructive; all other transitions are rapidly displacive. Geller provides evidence that the structure of phase XII is based on a spiral chain rather than the eight-membered ring, found in the rhombic form; this appears consistent with the observations that field XII is in the high-pressure and high-temperature region of the phase diagram. The complexity of the diagram at lower pressure and temperature is not surprising in that structures utilizing the eight-membered, puckered-ring sulfur molecules, bound to each other essentially by van der Waals forces, would seem to allow for a variety of phase changes without necessarily requiring the breaking of strong covalent bonds.

There is a possibility that the XI-XII boundary should be actually somewhat lower because at temperatures along this boundary the reaction is very slow; longer runs might have permitted recognition of the reaction. How much the boundary would be lowered is not known, but after runs of 83 days duration it did not drop down to 165°C at 36 kb.

Transitions from about 120° to 140°C were detected by volumetric and optical techniques up to pressures of about 56 kb. By DTA methods, Bell *et al.* (*7*) found a transition at slightly lower temperatures, extending from atmospheric pressure to 20 kb, which they attributed to the solid-liquid equilibrium boundary. They placed the rhombic-monoclinic-liquid triple point at 2.5 kb and 107°C. In our experiments, the transitions at 120° to 140°C, up to about 26 kb, are accompanied by volume increases. We believe it unlikely that the high-temperature phases along this boundary, if actually liquid, could be held in their stability fields by our piston-cylinder type of apparatus, even if the liquids were highly viscous. A liquid under such conditions would blow out of the cylinder in a manner similar to the violent rapid extrusions encountered in the volumetric apparatus, when what we interpret to be the liquidus is eventually reached. Quench experiments from fields IV and VI to room conditions yield a yellow brittle material which gives the x-ray diffraction pattern of rhombic sulfur. On the other hand, the product quenched from above our liquidus (agreeing in general with the liquidus reported by several workers) and examined immediately is a viscous liquid. Moreover, according to Tammann (*12*), the rhombic-monoclinic-liquid triple point occurs at 1294 bars and 151°C, and the monoclinic-liquid equilibrium boundary has a positive slope.

In addition to the evidence on stability fields for 12 crystalline high-pressure forms of sulfur, we have identified four different high-pressure sulfur liquids below 30 kb (*13*); data for our melting curve have been compared with those of other investigators (*14*).

GARY C. VEZZOLI
FRANK DACHILLE
RUSTUM ROY

Materials Research Laboratory,
Pennsylvania State University,
University Park 16802

References and Notes

1. T. Baak, *Science* **148**, 1220 (1965).
2. S. Geller, *ibid.* **152**, 644 (196→ *ibid.* **161**, 290 (1968).
3. C. B. Sclar, L. C. Garrison, W. B. Gager, O. M. Stewart, *Phys. Chem. Solids* **27**, 1339 (1966).
4. I. E. Paukov, E. Yu. Tonkov, D. S. Mirinskiy, *Dokl. Akad. Nauk SSSR* **164**, 588 (1965).
5. C. Susse, R. Epain, B. Vodar, *J. Chim. Phys.* **63**, 1504 (1966).
6. K. Ward and B. Deaton, *Phys. Rev.* **153**, 947 (1967).
7. P. M. Bell, J. C. England, G. Kullerud, *Carnegie Inst. Wash. Year B.* **65**, 354 (1965–1966); B. C. Deaton and F. A. Blum, *Phys. Rev.* **137**, A1131 (1964); H. Rose and O. Mügge, *Neues Jahrb. Mineral. Geol. Palaeontol.* **48**, 250 (1923).
8. F. Dachille and R. Roy, in *The Physics and Chemistry of High Pressures* (Society of Chemical Industry, London, 1962), p. 77.
9. C. H. Bates, *Penn. State Univ. Mater. Res. Lab. Tech. Rep. No. 22* (1966), p. 31 [contract No. Nonr 656(20)].
10. G. C. Vezzoli, thesis, Pennsylvania State University (1969).
11. W. Basset, T. Takahashi, P. Stook, *Rev. Sci. Instrum.* **38** (1), 37 (1967).
12. G. Tammann, *Ann. Phys.* **3**, 178 (1900).
13. G. C. Vezzoli, F. Dachille, R. Roy, *J. Polymer Sci.*, in press.
14. ———, *Inorg. Chem.*, in press.
15. A. Pinkus, J. Kim, J. McAtee, Jr., C. Concilio, *J. Amer. Chem. Soc.* **81**, 2652 (1959).
16. Supported by NSF grant GK-1686X.

12 November 1968; revised 4 June 1969 ■

Galactic Water Vapor Emission: Further Observations of Variability

Abstract. *Recent observations of the 1.35-centimeter line emission of water vapor from galactic sources show short-term variability in the spectra of several sources. Two additional sources, Cygnus 1 and NGC 6334N, have been observed, and the spectra of W49 and VY Canis Majoris were measured over a wider range of radial velocity.*

After the discovery of the 1.35-cm line emission of water vapor from four galactic sources (*1*), observations made with higher telescope resolution (*2*) showed intense radiation from eight galactic source regions of small diameter. Pronounced variations in the spectrum of the source region associated with W49 were observed over a few weeks' time (*2*). The observation of such short-term variability is critical to the understanding of the regions of water vapor emission and implies a very small diameter for the emitting region. We have made new observations between 15 March and 9 April 1969, using the 85-foot (26-m) reflector at the Naval Research Laboratory's Maryland Point Observatory and spectral-line radiometer system described in our previous paper (*2*). Spectra were measured with a spectral resolution of 4 khz except for the very wide spectrum of W49 (Fig. 1), which was measured with a resolution of 100 khz. The level of fluctuation in random noise had a root-mean-square value of 10°K for the 4-khz spectra and 3°K for the 100-khz spectrum. Additional fluctuations due to the gain calibration with a noise source of 90°K are present in strong spectral features. The observed antenna temperatures have been corrected for atmospheric absorption ranging from 10 to 30 percent and are accurate to about 10 percent except for the noise-limited weak features. No correction has been applied for changes of antenna gain with zenith angle; this would affect significantly only those sources at large negative declinations. This correction is not accurately known, but it may be as large as 15 to 20 percent at a declination (δ) of −30°. Unless otherwise specified, the observations were made with linear polarization at a position angle of 0°.

The observations show further time variations in the spectrum of W49, variations in the spectra of the source region associated with the Orion Nebula, the thermal radio source G133.7 + 1.2 (W3), and W75S, and a probable change in the spectrum of G0.7 − 0.0 (Sagittarius B2). Water vapor emission was observed from the OH emission source, Cygnus 1, discovered by Ellder *et al.* (*3*). We have also observed H_2O emission from NGC 6334N and from the additional feature at + 37 km/sec in the spectrum of VY Canis Majoris, both of which were observed by Meeks *et al.* (*4*).

All radial velocities reported by Knowles *et al.* (*2*) were referred to a nominal laboratory frequency of 22235.22 Mhz as given in the National Bureau of Standards tables (*5*). The results given here are referred to a probably more accurate rest frequency of 22235.08 Mhz, which is the weighted mean of the frequencies of the hyperfine components of the transitions from the 6_{16} to 5_{23} levels as measured by Bluyssen *et al.* (*6*). The radial velocity scales presented here are therefore shifted by 1.9 km/sec toward more positive velocity than those in the previous report (*2*), and the radial velocities of the observed components appear shifted by 1.9 km/sec toward more negative velocity than those reported earlier (*2*).

Typical spectra of the source region associated with W49, measured at intervals of about a month from 19 January to 6 April 1969, are shown in Fig. 2. The two intense lines at + 7 and + 14 km/sec, which disappeared between 25 January and 8 February 1969, have not reappeared. However, during late March and early April an intense line developed at + 9 km/sec, the same velocity as the third feature which disappeared in early February. In addition, the features at radial velocities of − 6 and + 25 km/sec have both decreased in intensity while others have increased. Two pairs of lines, the (+ 7 km/sec, + 14 km/sec) pair and the (− 6 km/sec, + 25 km/sec) pair, change intensity together and are roughly symmetrical about the strong feature at + 10 km/sec. This suggests some sort of association involving the components of the pairs and the possibility of ordered motions of the emitting gas clouds. In our previous paper (*2*) we mentioned that the spectrum of the W49 source extended to a radial velocity of − 150 km/sec. This finding was confirmed by Meeks *et al.* (*4*). A wide-range spectrum of the W49 source measured with 100-khz resolution in early April is shown in Fig. 1. We did not observe the intense feature at + 140