Magnetic Susceptibilities of Sulfur, Selenium and Tellurium from Room Temperature to 1100°C

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(Received August 18, 1959)

The temperature-dependences of magnetic susceptibilities of sulfur, selenium and tellurium have, hitherto, been investigated by many workers. Some different results can, however, be found among their data. The magnetic susceptibilities of the three elements have, therefore, been measured with the recording magnetic balance to compare the present results with those reported by other investigators and to compare the present results with experimental results observed on the physical properties such as viscosity, specific heat, electrical conductivity and so on.

Experimental

Materials.—*Sulfur.* — Guaranteed sulfur, Kanto Chemical Co. Ltd., was purified by Bacon and Fanelli's procedure[1], and then was treated by Gardner and Fraenkel's method[2] to eliminate magnetic impurities.

Selenium.—Guaranteed selenium, Junsei Chemical Co. Ltd., was distilled several times under high vacuum to obtain selenium of spectro grade. A glassy solidified black-selenium (glassy selenium) was prepared by quenching a sample of molten selenium under vacuum of 10^{-5} mmHg. This sample was confirmed to have diffused rings without diffraction patterns by X-ray analysis. Hexagonal selenium was obtained by heating a sample of glassy selenium at about 130°C for 48 hr. under vacuum of 10^{-5} mmHg. This sample was found to have hexagonal patterns.

Tellurium.—Tellurium of Merck (sample A) and a specimen produced by Mitsubishi Ōsaka Refinery (sample B) were distilled three and five times, respectively, to obtain tellurium of spectro grade. Both the samples were crystallized by cooling very slowly from the molten state under vacuum of 10^{-5} mmHg. It was ascertained by X-ray examinations that both the samples had hexagonal patterns.

Measurements.—Measurements were carried out by using the recording magnetic balance described in detail in the previous report[3]. The dimension of the sample bulb was the same as the previously reported one. The apparatus, which was operated by the Faraday method, was modulated on a recording chart to be able to indicate the changes of

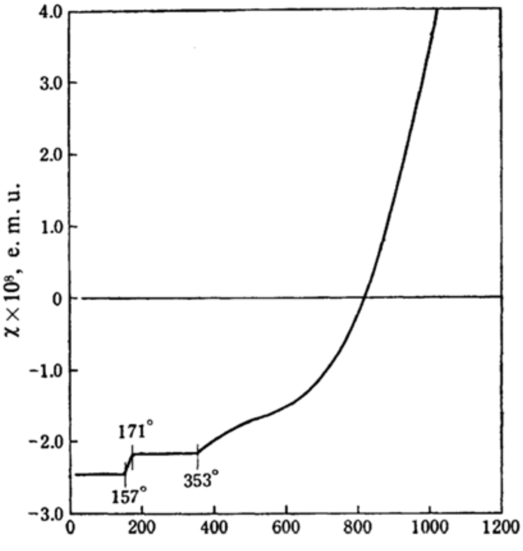

Fig. 1. Magnetic susceptibility-temperature curve for sulfur (50.2 mg. in weight).

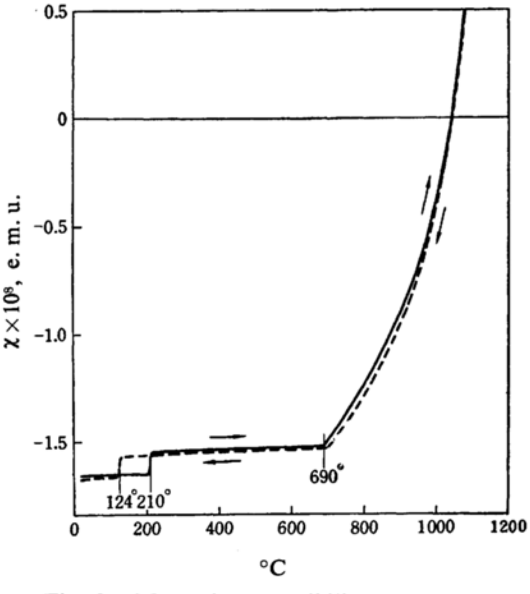

Fig. 2. Magnetic susceptibility-temperature curve for glassy selenium (50.0 mg. in weight).
—— heating ---- cooling

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[1] R. F. Bacon and R. Fanelli, *J. Am. Chem. Soc.*, **65**, 639 (1943).

[2] D. M. Gardner and G. K. Fraenkel, ibid., **76**, 5891 (1954); ibid., **78**, 3279 (1956).

[3] S. Tobisawa, This Bulletin, **32**, 1173 (1959).

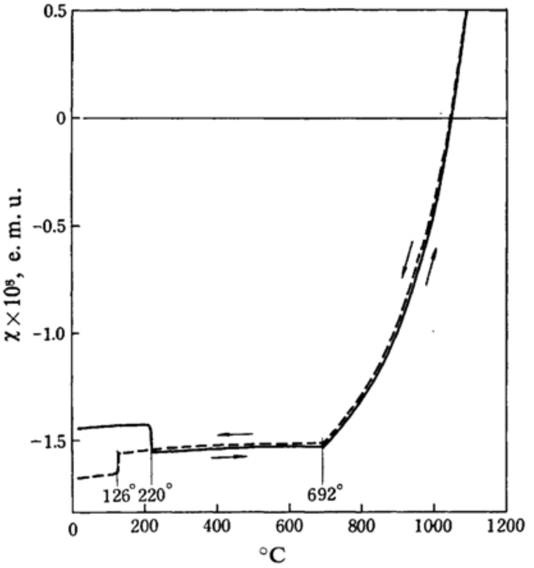

Fig. 3. Magnetic susceptibility-temperature curve for hexagonal selenium (50.2 mg. in weight).
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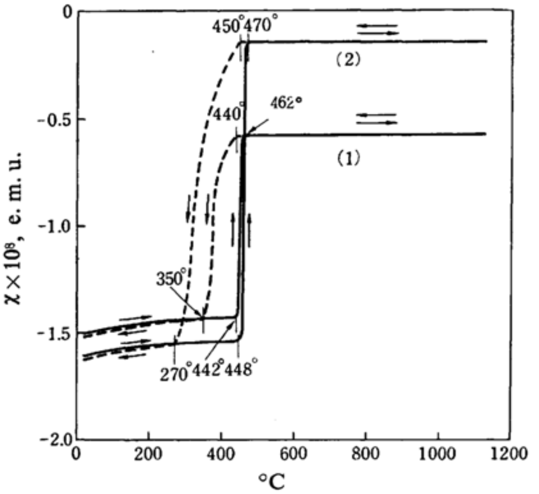

Fig. 4. Magnetic susceptibility-temperature curves for hexagonal tellurium.
(1) sample A (50.0 mg. in weight).
(2) sample B (50.1 mg. in weight).
—— heating ---- cooling

0.1 mA, which corresponded to -1.3×10^{-9} e.m.u. in magnetic susceptibility. In each experiment, a sample of about 50 mg. was charged into a fused quartz bulb. This bulb was sealed carefully, after having been evacuated to about 10^{-5} mmHg. The measurements were made with heating or cooling rates of 300°C per hour, at constant field, 8250 Oersteds. The results obtained are shown in Figs. 1—4.

Results

Comparison with the Results Obtained by other Investigators.—*On the Solid State.*—The magnetic susceptibilities of the three elements obtained at room temperature are given in Table I. The susceptibility of sulfur scarcely changes with temperature, while those of selenium and tellurium change slightly with temperature.

TABLE I. THE MAGNETIC SUSCEPTIBILITIES OF THE THREE ELEMENTS

Sample	$\chi\times10^6$ (per g.)
Sulfur	-0.49
Glassy selenium	-0.33
Hexagonal selenium	-0.29
Hexagonal tellurium	-0.30 (Sample A) -0.32 (Sample B)

On the Behavior of Susceptibilities at the Melting Points and their Neighborhood.—(1) The susceptibility of sulfur showed no particular changes at the melting point and its neighborhood. It began to decrease from 157°C, and reached -0.43×10^{-6} per g. at 171°C. Ishiwara⁴⁾ reported that the susceptibility of sulfur decreased at about 160°C, while Honda⁵⁾ showed that the susceptibility of sulfur had a minimum value at the melting point.

(2) Busch et al.⁶⁾ reported that the volume susceptibility of hexagonal selenium increased on fusion. In Figs. 2 and 3, the susceptibility of glassy selenium decreased slightly at 210°C, while that of hexagonal selenium increased slightly at 220°C. On cooling, both kinds of liquid selenium turned to glassy selenium, showing slight increases in susceptibilities at about 125°C under the present experimental condition. Busch et al. reported that the volume susceptibility of glassy selenium had no abrupt changes despite the fast cooling of molten selenium.

(3) The susceptibility of hexagonal tellurium of sample A began to decrease at 442°C and reached the value of -0.12×10^{-6} per g. at 462°C. The susceptibility of sample B began to decrease at 448°C and reached the value of -0.03×10^{-6} per g. at 470°C. The susceptibility-temperature curve for hexagonal tellurium deflected toward sides opposite to that for hexagonal selenium, as shown in Figs. 3 and 4. Under the present experimental condition, sample A was supercooled to 350°C, while sample B was supercooled to 270°C.

In the Liquid State.—(1) The susceptibility

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4) T. Ishiwara, *Science Repts. Tōhoku Imp. Univ.*, 9, 233 (1920).

5) K. Honda, ibid., 1, 1 (1911).

6) G. Busch and O. Vogt, *Helv. Phys. Acta*, 30, 224 (1957).

of liquid sulfur scarcely changed until 353°C (-0.43×10^{-6} per g.).

(2) The susceptibility of fused selenium, -0.31×10^{-6} per g. at 220°C, decreased slightly with temperature. The values reported as the susceptibility of fused selenium are as follows: -0.31×10^{-6} 7), -0.304×10^{-6} 8) and -0.32×10^{-6} per g.9) Busch et al.6) showed that the volume susceptibility of fused selenium was -1.347×10^{-6} per cc. at the melting point. Taking 3.987 g. per cm^3 10) as the density of fused selenium at 220°C, Busch's value corresponded to -0.338×10^{-6} per g. in mass susceptibility. This value is greater than the present experimental value at 220°C.

(3) The value of liquid tellurium from sample B at 470°C, -0.03×10^{-6} per g., consistent with the values of liquid tellurium obtained by Honda11) and Endo12), was smaller than that of sample A. On the other hand, values reported as the volume susceptibility of liquid tellurium by the other authors were -0.3×10^{-6} 13) and -0.767×10^{-6} 6) per cc.

In the Higher Temperature Range.—(1) The curve in Fig. 1 deflected toward paramagnetic sides above 353°C. Néel14) and Scott15) reported that the diatomic sulfur molecule produced by the dissociation of sulfur at high temperature, was paramagnetic. On the assumption that the deflection toward paramagnetic sides above 353°C is due to the paramagnetism of the diatomic sulfur molecule, an attempt was made to estimate the weight of the diatomic sulfur molecule at every temperature by comparing the experimental value of paramagnetic susceptibility with the value calculated from Van Vleck's equation16). The ratios of the weight of the diatomic sulfur molecule to the total weight of sulfur at every temperature, are shown in Fig. 5.

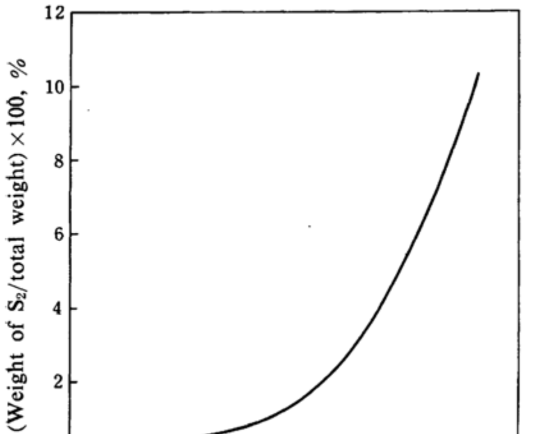

Fig. 5. (Weight of S_2/total weight)-temperature curve for sulfur.

(2) From Figs. 2 and 3, it is clear that selenium shows paramagnetism above 690°C and that the paramagnetic change occurs reversibly with temperature. Bhatnagar et al.17) found that selenium vapor as well as sulfur vapor was paramagnetic. The ratio of the weight of the diatomic selenium molecule to the total weight of selenium was estimated in the same way as that used for sulfur. The results are given in Fig. 6.

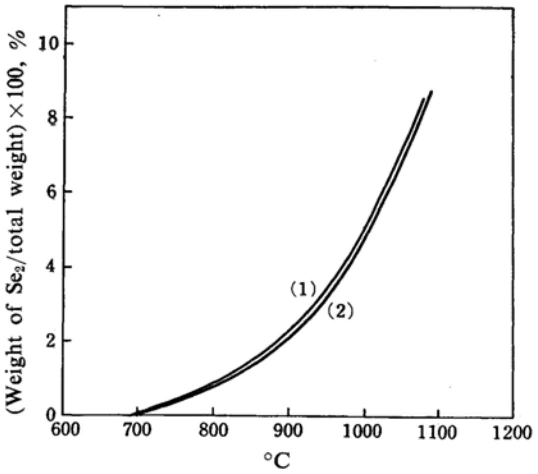

Fig. 6. (Weight of Se_2/total weight)-temperature curve for selenium.
(1) for glassy selenium.
(2) for hexagonal selenium.

(3) In contrast with sulfur and selenium, tellurium showed no paramagnetic changes until 1100°C under the present experimental condition. On the other hand, Busch et al. reported that tellurium was paramagnetic above 980°K.

Reference to Experimental Results Observed on the Physical Properties such as Viscosity, Specific Heat, Electrical Conductivity and so on.

—*Sulfur.*—It is well known that liquid sulfur

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7) P. Curie, *Ann. de Chem. et Phys.*, **5**, 289 (1895).

8) K. Honda and T. Sone, *Science Repts. Tōhoku Imp. Univ.*, **2**, 25 (1913).

9) M. Owen, *Ann. Physik*, **37**, 657 (1912).

10) S. Dobinski and J. Wesolowski, *Bull. intern. acad. polon. sci., Classe sci. math. nat.* **No. 8-9A**, 446 (1936).

11) K. Honda, *Ann. Physik*, **32**, 1027 (1910).

12) H. Endo, *Science Repts. Tōhoku Imp. Univ.*, **16**, 206 (1927).

13) S. R. Rao and S. R. Govindarajan, *Proc. Indian Acad. Sci.*, **10A**, 235 (1939).

14) L. Néel, *Compt. rend.*, **194**, 2035 (1932).

15) A. B. Scott, *J. Am. Chem. Soc.*, **71**, 3145 (1949).

16) J. H. Van Vleck, "Electric and Magnetic Susceptibilities", Oxford University Press, Oxford, London (1937), p. 266.

17) S. S. Bhatnagar, H. Lessheim and M. L. Khanna, *Proc. Indian Acad. Sci.*, **6A**, 155 (1937); *Nature*, **140**, 152 (1938).

has anomalies in regard to the physical properties such as viscosity[1,18,19], specific heat[20] and others[19,21] in the vicinity of 160°C. Gee[22] has interpreted these anomalies from the standpoint of the equilibrium between eight-membered sulfur rings and long chain polymers. Gee and his colaborators[23] measured the susceptibility of sulfur to investigate the existence and concentration of free radicals. They could not find any paramagnetic contribution from free radicals. On the other hand, Gardner et al.[2] confirmed the paramagnetism due to free radicals by the paramagnetic resonance absorption measurements over the range from 189° to 414°C, and stated that the paramagnetism increased reversibly with temperature. From the comparison of the present results with various results mentioned above, it can be concluded that the change in susceptibility of liquid sulfur at 157 ~171°C suggests the formation of free radicals due to the scission of the eight-membered sulfur rings. Therefore, it is reasonable to suppose from the curve in Fig. 1 that there occurred no scission of the eight-membered sulfur rings from the melting point to 157°C. Also no scission was acceptable in the temperature range from 171° to 353°C, because the curve in Fig. 1 showed no change in this range. The results mentioned above are supported by the fact that the maximum viscosity of liquid sulfur decreased rapidly with temperature in the corresponding range.

Selenium.—The change in susceptibility of hexagonal selenium at 220°C is due to phase transition on fusion, because the melting point of hexagonal selenium reported in the literature is 217.4°[24] or 220.2°C[25]. On the contrary, it is known that glassy selenium has no definite melting point. By X-ray investigations Lark-Horovitz[26] has concluded that glassy selenium consists of supercooled liquid, and that the chain structure was preserved in the liquid states. On the other hand, from X-ray analysis Krebs[27] insists that about one-third of glassy selenium is in the form of eight-membered selenium ring and the rest in poly-membered ring with about one thousand selenium atoms. From the electrical measurements on selenium, glassy selenium is an insulator and liquid selenium is a semiconductor with predominant hole conduction[28]. According to Krebs' interpretation, this difference between the electrical properties for glassy and liquid selenium can be ascribed to the difference between ring structure of glassy selenium and the chain structure of liquid selenium. It is reasonable to conclude that the decrease in susceptibility of glassy selenium at about 210°C can be attributed to the scission of selenium rings similar to the scission of sulfur at 157~171°C, and that the increases in susceptibilities of liquid selenium at about 125°C on cooling are related to the reclosing of chains into rings. No scission was acceptable in the temperature range from 220° to 690°C, because the susceptibility-temperature curves for selenium in Figs. 2 and 3 showed no abrupt changes in this temperature range. This interpretation is supported by the fact that the viscosity of liquid selenium decreases smoothly with temperature, showing no scission of rings[29].

Tellurium.—Umino[30] reported an anomaly in specific heat of solid tellurium. By X-ray investigations of tellurium layers in vacuo, Scanlon et al.[31] showed that no structure change of solid tellurium occurred up to fusion. In Fig. 4, the susceptibility-temperature curves for solid tellurium showed no abrupt changes.

Epstein et al.[32] showed that the electrical resistivity, the Hall coefficient and the thermoelectric power of tellurium decreased at the melting point of 445°C. Busch et al.[6] stated that the volume susceptibility of tellurium decreased abruptly together with the decreases in the electrical resistivity, the Hall coefficient and the thermoelectric power. In Fig. 4, the susceptibilities of samples A and B decreased in the ranges from 442° to 462°C and from 448° to 470°C, respectively. On the other hand, as the melting point of tellurium, diversely discordant values from 420° to 455°C have been listed by Machol et al.[33] The results of X-ray investigations[34] on tellurium

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[18] C. Farr and D. B. Macleod, *Proc. Roy. Soc.*, **A118**, 534 (1928).

[19] J. Schenk, *Physica*, **23**, 546 (1957).

[20] H. Braune and O. Möller, *Z. Naturforsch.*, **9a**, 210 (1954).

[21] A. M. Kellas, *J. Chem. Soc.*, **113**, 903 (1918).

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[23] F. Fairbrother, G. Gee and G. T. Merrall, *J. Polymer Sci.*, **16**, 459 (1955).

[24] L. E. Dodd, *J. Am. Chem. Soc.*, **42**, 1579 (1920).

[25] E. Berger, *Z. anorg. Chem.*, **85**, 75 (1914).

[26] K. Lark-Horovitz and E. P. Miller, *Phys. Rev.*, **51**, 380 (1937).

[27] H. Krebs, "Semiconducting Materials", Butterworths, London (1951), p. 246; H. Krebs and F. Schultze-Gebhardt, *Naturwissenschaften*, **41**, 474 (1954); *Acta Cryst.*, **8**, 412 (1955).

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[29] S. Dobinski and J. Wesolouski, *Bull. intern. acad. polon. sci., Classe sci. math. nat.*, **No. 10A**, 7 (1937).

[30] S. Umino, *Kinzoku-no-kenkyu*, **3**, 498 (1926).

[31] W. Scanlon and K. Lark-Horovitz, *Phys. Rev.*, **72**, 530 (1947).

[32] A. S. Epstein, H. Fritzsche and K. Lark-Horovitz, ibid., **107**, 412 (1957).

[33] R. E. Machol and E. F. Westrum, *J. Phys. Chem.*, **62**, 361 (1958).

[34] R. Buschert, I. G. Geib and K. Lark-Horovitz, *Phys. Rev.*, **98**, 1157 (1955).

immediately after fusion have shown that the number of nearest neighbors and the distance between the nearest neighbors determined for the crystal persist in the liquid state. This indicates the existence of chain molecules bound by covalent bonds in the liquid. The results of electrical investigations[28,32,35] on tellurium have shown that liquid tellurium shows a semiconducting property in which hole conduction is predominant, and that the semiconductor-metal transition occurs gradually at higher temperatures. From the results of electrical measurements Epstein et al. stated that tellurium atoms bound by covalent bonds into chains of various lengths, tellurium ions, and free electrons will be present in liquid tellurium, and that, as the temperature increases, the chains will be ionized, giving off free electrons which leave behind holes, i. e., missing covalent bonds, which in turn are able to migrate within the chains, until very high temperatures are reached, at which the liquid will be composed of tellurium ions and free electrons. It can, therefore, be considered that the decrease of susceptibility during fusion in Fig. 4 is due to a paramagnetic contribution from unpaired spins produced by incomplete ionization of the valence shell[36]. That the susceptibilities of tellurium after fusion in Fig. 4 are independent of temperature, may be owing to the mixed effects of diamagnetic and paramagnetic contributions associated with the semiconductor-metal transition mentioned above.

Summary

(1) The susceptibility of sulfur showed the first change at about 157°C, showing no changes at the melting point and its neighborhood. The change is attributed to the radical chains owing to the scission of eight-membered sulfur rings.

(2) On fusion the susceptibility-temperature curve for glassy selenium deflected toward sides opposite to that for hexagonal selenium. It is considered that the decrease in susceptibility of glassy selenium can be ascribed to free radicals produced by the scission of selenium rings. On cooling, liquid selenium turned to glassy selenium, showing the increase in susceptibility at about 125°C. It can be considered that this change is related to the reclosing of chains into rings.

(3) The susceptibility of hexagonal tellurium decreased abruptly on fusion. It may be considered that this change is due to a paramagnetic contribution from unpaired spins produced by incomplete ionization of the valence shell.

(4) The susceptibility-temperature curves for sulfur and selenium were deflected toward paramagnetic sides above 353° and 690°C, respectively. The paramagnetism increased reversibly with temperature, while the susceptibility of tellurium was independent of temperature to 1100°C. On sulfur and selenium, the ratios of the weight of the diatomic molecule to the total weight at every temperature were obtained from the weight of the diatomic molecule estimated by comparing the experimental value of paramagnetic susceptibility with the value calculated from Van Vleck's equation.

The author wishes to express his sincere gratitude to Professor Y. Nomura for his helpful suggestions and encouragement in the course of this work. The author is also indebted to Mr. T. Ashida for his valuable assistance in X-ray analysis and to Mr. S. Uchida for his kind assistance.

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