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Infrared Absorption and Oxygen Content in Silicon and Germanium

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An optical absorption band at 9μ has been correlated with the oxygen content in silicon. Pulled silicon crystals were found to contain up to 10^{18} oxygen atoms per cm^3 which seem to originate from the quartz crucible. The oxygen concentration in silicon crystals prepared by the floating zone technique in vacuum was found to be less than 10^{16} oxygen atoms per cm^3. The 9μ absorption due to silicon-oxygen bond stretching vibrations provides a possibility for a quantitative oxygen analysis of high sensitivity. A corresponding absorption in germanium at 11.6μ is believed to be due to a germanium-oxygen vibration.

INTRODUCTION

At wavelengths greater than 1.2μ, pure silicon is highly transparent, as is pure germanium at wavelengths above 1.8μ.[1] Bands in silicon due to lattice absorption occur within the range of from 8μ to 25μ and in germanium from 11μ to 35μ.[2,3] There may be additional absorption superimposed because of the presence of free charge carriers,[4] but it can be disregarded in this study since we are dealing with samples having high resistivity. An absorption band at 9μ is a common occurrence in silicon[1–3] and some investigators have surmised that it is the result of oxygen, while others consider it to be a lattice band. Silicon crystallized by the floating zone technique,[5] which requires no quartz crucible, showed at 9μ a greatly reduced absorption.[6] It is this band and a corresponding absorption in germanium which we have investigated.

EXPERIMENTAL

Using a Perkin-Elmer double-pass spectrometer, absorption measurements of a variety of high-purity silicon samples were made in a wavelength range around 9μ. The samples were optically polished and by measuring different thicknesses it was verified that the observed absorption is a bulk effect and not a surface phenomenon. Table I is a list of typical samples measured, giving their characteristics and absorption coefficient at 9μ.

It will be noted that, without exception, samples melted in a quartz crucible displayed a higher absorption coefficient than the silicon samples crystallized without a crucible.

The results of three crucial experiments are also given in Table I. A section of sample 105, which displayed an absorption of 1.05 cm^{-1} originally, increased its absorption to 1.55 when melted for twenty minutes in the floating zone equipment under an oxygen atmosphere at a pressure of 1 mm Hg. During this experiment, the silicon reacted strongly with the oxygen, depositing a thick coat of silicon monoxide on the cold walls of the melting chamber. In a second experiment a section of sample 85, pulled originally from a quartz crucible and then melted in high vacuum for thirty minutes, by means of the floating zone technique, showed a decrease in absorption by a factor of three. In the third experiment the same decrease in the 9μ absorption was observed with sample 84 after several passes of the floating zone.

The 9μ absorption band was also investigated at low temperature. A comparison of the results obtained with samples 13 and 109 at room temperature and at 90°K is shown in Figs. 1 and 2. It will be noted that the absorption of sample 13, which was pulled from a quartz crucible, shifts to shorter wavelengths, sharpens, and develops a fine structure,[7] whereas the weak absorption of sample 109, prepared by the floating zone technique, decreases by a factor of approximately two.

TABLE I. Absorption coefficient at 9μ of different silicon samples.

Sample No.	Origin and preparation[a]	Absorption coeff. at 9 microns	Remarks
104	*FM*, *QC*, *S*	3.2 cm^{-1}	47 ohm cm
13	*DP*, *QC*, *S*	3.6 cm^{-1}	6 ohm cm
08	*DP*, *QC*, *P*	4.5 cm^{-1}	10 ohm cm "densified silicon"
98	*FM*, *FZ*, *S*	1.05 cm^{-1}	70 ohm cm
109	*DP*, *FZ*, *S*	1.05 cm^{-1}	35 ohm cm
06	*FM*, *P*	~1.0 cm^{-1}	Microcrystalline, as deposited on the tantalum wire
105	*FM*, *FZ*, *P*	1.05 cm^{-1}	Originally
		1.55 cm^{-1}	*FZ* in oxygen of 1 mm Hg
85	*DP*, *QC*, *P*	4.2 cm^{-1}	20 ohm cm
		1.3 cm^{-1}	Melted in vacuum
84	*DP*, *QC*, *P*	4.2 cm^{-1}	20 ohm cm
	DP, *FZ*, *P*	1.3 cm^{-1}	After several *FZ* passes, 40 ohm cm

[a] *DP* = silicon from DuPont (zinc reduction process), *FM* = silicon from Foote Mineral Company (iodide process), *QC* = crystallized from quartz crucible, *FZ* = crystallized by floating zone technique, *S* = single crystal, *P* = polycrystalline.

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[1] H. Y. Fan and M. Becker, *Proceedings of the Reading Conference* (Butterworths Scientific Publications, London, 1951).

[2] R. J. Collins and H. Y. Fan, Phys. Rev. **93**, 674 (1954).

[3] M. Lax and E. Burstein, Phys. Rev. **97**, 39 (1955).

[4] H. B. Briggs, Phys. Rev. **77**, 727 (1950); H. Y. Fan and M. Becker, Phys. Rev. **78**, 178 (1950); H. B. Briggs and R. C. Fletcher, Phys. Rev. **91**, 1342 (1952); Kaiser, Collins, and Fan, Phys. Rev. **91**, 1380 (1953).

[5] P. H. Keck, Physica **20**, 1059 (1954).

[6] According to a private communication by H. F. Priest (to be published).

[7] This is in agreement with a fine structure observed in silicates. A. Schaefer and F. Matossi, *Das Ultrarate Spektrum* (Verlag Julius Springer, Berlin, 1930).

All samples marked *QC* in Table I were pulled in an inert atmosphere. A crystal pulled in vacuum indicated a smaller absorption at 9μ, however, at 90°K a striking difference between this sample and the floating zone samples still remained.

For comparison purposes, the absorption within the 9μ range was measured on thin SiO_2 films which were prepared by evaporation of SiO in vacuum onto cleaved sodium chloride surfaces and subsequently oxidized. The maximum of the absorption band of SiO was found to occur at 10μ and upon oxidation, shifted to 9.3μ. The results are in agreement with the findings of Hass and Salzberg.[8]

DISCUSSION

It is known that quartz reacts with molten silicon[9] to form gaseous SiO. This in turn may dissolve in silicon to a certain extent. Upon crystallization we expect that oxygen will enter the silicon lattice interstitially and will be bound to silicon. The 9μ absorption band observed in silicon may be explained then as a silicon oxygen vibration similar to the vibrations in silica and in all quartz modifications.[10,11]

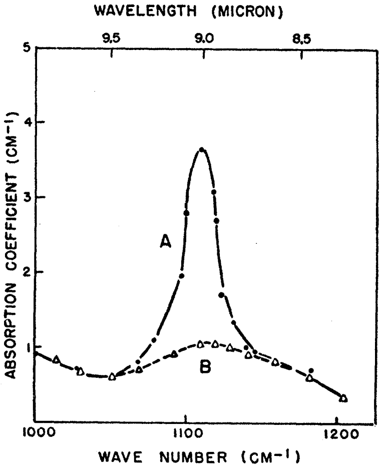

FIG. 1. Absorption coefficient of silicon at room temperature. *A* (sample 13) pulled from a quartz crucible, *B* (sample 109) prepared by floating zone technique.

Furthermore, the experiment with the recrystallization of sample 105 in an oxygen atmosphere indicates that the increased absorption is caused by oxygen. On the other hand, there is no doubt that oxygen can be removed from silicon by melting it in vacuum, without the use of a quartz crucible. This fact is noted as a result of the experiments with samples 84 and 85 in which the 9μ absorption band decreased.

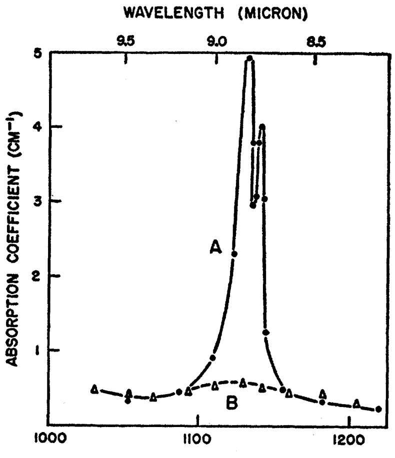

FIG. 2. Absorption coefficient of silicon at 90°K. *A* (sample 13) pulled from a quartz crucible, *B* (sample 109) prepared by floating zone technique.

The most conclusive results can be derived from the correlation of the 9μ absorption band with the quantitative oxygen analysis.[12] Data obtained on four samples are listed in Table II, columns 2 and 4. It will be noted that the absorption is proportional to the oxygen concentration, within the limit of accuracy of the vacuum fusion analysis.

Spectrochemical analysis of the silicon samples investigated did not reveal any detectable metallic impurities. This result implies that in the pulled samples the concentration of such impurities is much smaller than that of oxygen. The major part of oxygen, therefore, cannot be bound to impurities but must be attached to silicon, as indicated by the absorption at 9μ.

From the curves (Figs. 1 and 2) it can be inferred that not only the amount, but also the cause of the absorption, is different for the two samples 13 and 109. The uniform decrease of the absorption, with decrease in temperature observed in the floating zone sample 109 is in good agreement with the previously observed decrease of the lattice absorption with temperature.[2] Thus it might be concluded that curve *B* in Fig. 1 and curve *B* in Fig. 2 correspond essentially to a lattice absorption. Oxygen in sample 109 cannot be detected by the 9μ measurement. Sample 13, which was pulled from a silica crucible, gave very different results. The narrowing and shifting of the absorption peak, as the temperature decreases, is very similar to the change reported for fused quartz.[11] This similarity further supports the assumption that in this case the absorption is due to a silicon-oxygen vibration. It is interesting to note, that the areas between the absorption curves *A*

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[8] G. Hass and C. D. Salzberg, J. Opt. Soc. Am. **44**, 181 (1954).

[9] H. N. Potter, Trans. Am. Electrochem. Soc. **12**, 191 (1907); K. F. Bonhoeffer, Z. physik Chem. **131**, 363 (1928); E. Zintl *et al.*, Z. anorg. u. allgemeine Chem. **245**, 1 (1940); H. Koenig, Optik **3**, 419 (1948); L. Brewer and R. K. Edwards, J. Chem. Phys **58**, 351 (1954).

[10] Schaefer, Matossi, and Wirtz, Z. Physik **89**, 210 (1934); F. Matossi and H. Krueger, Z. Physik **99**, 1 (1936).

[11] I. Simon and H. O. McMahon, J. Chem. Phys. **21**, 23 (1953).

[12] We are indebted to W. H. Smith of the General Electric Research Laboratory for having determined the oxygen concentration by vacuum fusion.

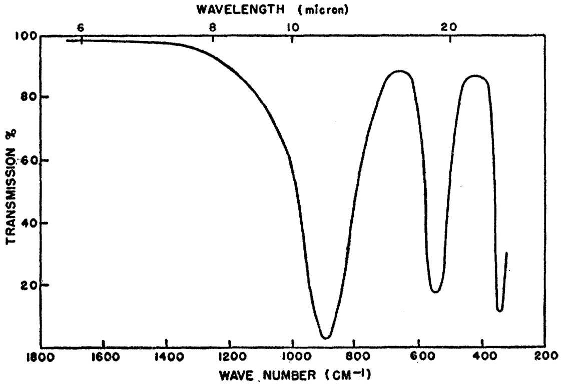

FIG. 3. Transmission of hexagonal GeO_2 measured on a KBr pellet containing GeO_2 powder.

and B (corresponding to the oxygen absorption only) remain constant, independent of temperature, indicating a Lorentz-type dispersion.

Optical absorption measurements at 9μ provide a method for a quantitative analysis of oxygen in silicon. The sensitivity of this analysis increases with decreasing temperature. The limit of detectability at liquid air temperature is approximately 10^{-5} weight percent oxygen or 10^{16} oxygen atoms per cm^3.

Most of the samples investigated were p-type. Since we are dealing here with a molecular vibration no apparent connection between the resistivity, conductivity type and the 9μ absorption can be expected.

Si-O BOND STRETCHING VIBRATION

Optical measurements on silicates and different modifications of SiO_2 led several investigators[10,11] to the conclusion that the absorption band, at approximately 9μ, is related to the Si—O bond stretching vibration. It is established that the frequency of the band maximum is affected very little even when there are drastic changes in environment. This fact would explain that we find very nearly the same resonance frequency in the silicon lattice. The distance between the silicon and oxygen atoms in silicates and quartz modifications is known to be 1.6 A. The following model could then be considered for silicon contaminated with small amounts of oxygen: Two neighboring silicon atoms give up their covalent bond and engage with an interstitial oxygen atom instead, forming an isosceles triangle with Si, O, Si at the corners. With Si—O distances of 1.6 A and assuming the Si—Si distance to be essentially unchanged (2.34 A), the bond angle Si—O—Si will be approximately 100°, which is quite feasible. Electronic neutrality is preserved in this model.

The number of Si—O oscillators can be estimated from the optical measurements as follows. For N_0 independent oscillators, having vibrational frequencies only, the area of the absorption band is given by the following equation[13]:

$$\int \alpha_\nu d\nu = N_0 \frac{\pi e^2}{3\mu c} \frac{(n^2+2)^2}{9n}. \tag{1}$$

α_ν is the absorption coefficient at the frequency ν, μ is the reduced mass of the oscillator, e is the net electronic charge, and n is the refractive index of the surrounding medium. For our estimate, the integral is approximated by the product of $\alpha_{\max}$, the absorption coefficient at the band maximum and H, the half-width of the band. Thus, we get

$$N_0 = \frac{9n}{(n^2+2)^2} \frac{3\mu c}{\pi e^2} \alpha_{\max} H. \tag{2}$$

First, we apply Eq. (2) to the absorption band at 9μ in silicon. With $\mu = 10.2$; $n = 3.6$; $e = 4.8 \times 10^{-10}$ esu and the experimental data for sample 85: $\alpha_{\max} = 3.2\ cm^{-1}$ and $H = 4.5 \times 10^{-3}$ ev, we find the number of oscillators

$$N_0 = 9.8 \times 10^{17}\ cm^{-3}.$$

Since each oxygen atom contributes two oscillators, the corresponding oxygen concentration would be $4.9 \times 10^{17}\ cm^{-3}$.

The agreement with the analytically determined number of oxygen atoms, $10.0 \times 10^{17}\ cm^{-3}$, is considered unexpectedly good, taking into consideration the assumptions made in Eq. (2), and also the fact that we used the full electronic charge, which is certainly too large for this type of covalent bond.

The fact that Eq. (2) gave reasonable results for the number of Si—O oscillators in silicon, seems to indicate small interactions between these oscillators and their environment. In our estimates, the factor $9n/(n^2+2)^2$ apparently provides a sufficiently accurate correction for the Lorentz "effective field."[14]

Equation (2) can also be applied to ionic crystals.[15] Thus we estimated the number of Si—O bonds in the amorphous quartz layers which had been prepared by the method described above. Our experiments gave

TABLE II. Comparison between the absorption coefficient at 9μ and the oxygen content of silicon. For history of samples, see Table I.

Sample No.	Total absorption coefficient at 9μ (cm^{-1})	Absorption coefficient due to oxygen (cm^{-1})	Vacuum fusion analysis. Weight percentage of oxygen $\times 10^{-4}$	Number of O-atoms	
				Vacuum fusion analysis (cm^{-3}) $\times 10^{17}$	Calculated from Eq. (2) (cm^{-3}) $\times 10^{17}$
109	1.05	...	3 ± 3	2.7	...
84	1.3	0.3	5 ± 3	4.5	0.5
104	3.2	2.2	8 ± 3	7.2	3.2
85	4.2	3.2	11 ± 3	10.0	4.9

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[13] R. E. Richards and W. R. Burton, Trans. Faraday Soc. **45**, 874 (1949).

[14] D. L. Dexter, Phys. Rev. **98**, 1533(A) (1955).

[15] B. Szigeti, Trans. Faraday Soc. **45**, 155 (1949); see also H. Froehlich, *Theory of Dielectrics* (Clarendon Press, Oxford, 1949).

$\alpha_{\max}=2.5\times10^4\ \text{cm}^{-1}$ and $H=10^{-2}$ ev for the 9μ band. Neglecting the strong dispersion in the 9μ range and taking $n=1.5$, we obtain for the number of oscillators $N_0=9\times10^{22}\ \text{cm}^{-3}$ or accordingly for the concentration of oxygen atoms $4.5\times10^{22}\ \text{cm}^{-3}$. On the other hand, the number of oxygen atoms in SiO_2 calculated from the density (2.3 g/cm^3) is $5\times10^{22}\ \text{cm}^{-3}$. Here again the agreement is unexpectedly good.

OXYGEN ABSORPTION IN GERMANIUM

Since we could find no information on the infrared spectrum of germanium dioxide in the literature, we prepared KBr-pellets containing GeO_2 powder (approximately 1 mg per cm^2 sample area). The hexagonal modification of GeO_2 used has the same structure as quartz. It will be noted in Fig. 3 that a very strong absorption band occurs at 11.5μ. This band is, we believe, a result of the Ge—O bond stretching vibration corresponding to the 9μ absorption in SiO_2. The frequency ratio at the absorption maxima in GeO_2 and SiO_2 is 1.3, which is somewhat larger than the ratio 1.1 of the square root of the reduced oscillator masses. The larger Ge—O distance compared with the Si—O distance may explain the difference.

Various germanium single crystals were measured in the wavelength range from 10μ to 14μ. Since the absorption coefficient in this range is very low, sample thicknesses up to several centimeters were employed to obtain a satisfactory accuracy. Three weak absorption bands at 11.8μ, 12.5μ, and 13.3μ were found to occur at room temperature in all samples. Measurements at 90°K revealed, however, a striking difference between samples having different genetic histories. While in crystals pulled from a graphite crucible the three bands decreased uniformly in intensity, some crystals pulled from a quartz crucible exhibited a small but sharp band at 11.6μ. Figure 4 shows a typical example of the absorption for a germanium specimen pulled from a quartz crucible. It seems that at low temperature a sharp band is superimposed on the short-wavelength side of the broad 11.8μ band. From this temperature behavior[2] we conclude that the three absorption bands found in all samples at room temperature are the result of lattice vibrations of germanium, while the sharp absorption peak at 11.16μ, revealed distinctly at 90°K, is explained as being the result of Ge—O bond stretching vibrations similar to the findings in Si. By assuming the oscillator strength of the oxygen-vibration in germanium to be the same as in silicon, the concentration of Ge—O bonds can be estimated. From the absorption at 11.6μ plotted in Fig. 4 we obtain an oxygen concentration which is two orders of magnitudes smaller than the oxygen concentration in the silicon sample 85, that is, approximately 10^{16} oxygen atoms per cm^3, while the germanium samples pulled from a graphite crucible are estimated to have less than 10^{15} oxygen atoms per cm^3 bound to germanium. Because of the smaller background absorption, the 11.6μ band in germanium is a more sensitive measure for the oxygen concentration than the 9μ absorption in silicon. At liquid air temperature, a concentration of the order of 10^{15} oxygen atoms per cm^3 or higher can be analyzed in germanium.

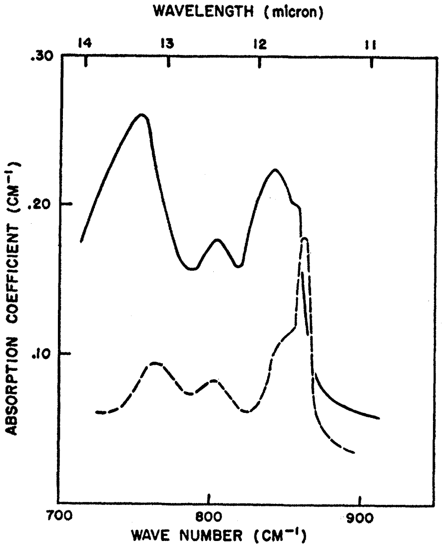

FIG. 4. Absorption coefficient of germanium pulled from a quartz crucible. Solid line 300°K, broken line 90°K.

If it is assumed that the oxygen originates from the quartz crucible, it is not surprising to encounter much smaller oxygen concentrations in germanium than are found in silicon, the melting point of germanium being much lower.

Unlike in silicon, the actual oxygen concentration in germanium can be considerably higher than calculated from the 11.6μ absorption, because oxygen may be bound to impurity elements which have a higher oxygen affinity than germanium.[16] In this case, the oxygen does not contribute to an absorption at 11.6μ.

CONCLUSIONS

Pulled silicon crystals display an absorption at 9μ which is caused by oxygen originating from the quartz crucible. A model is suggested in which oxygen atoms occupy interstitial positions and form bonds with two neighboring silicon atoms in the silicon lattice. Stretching vibrations of the resulting Si—O bonds are responsible for the observed 9μ absorption. Vacuum fusion analysis revealed oxygen concentrations up to 10^{18} atoms per cm^3 in pulled crystals. Assuming independent oscillators, good agreement was found between the oxygen analysis and an estimate of the concentration of Si—O bonds from the absorption data. The oxygen concentration in silicon prepared by the floating zone technique is at least hundred times lower than in

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[16] H. F. Priest (private communication).

crystals pulled from a quartz container. Optical absorption measurements at 9μ are suitable for a quantitative oxygen analysis in silicon. Oxygen-free silicon has a weak lattice absorption at 9μ.

A corresponding absorption at 11.6μ in germanium, due to Ge—O stretching oscillations, was found to be superimposed above a weak lattice band.

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Radiation Damage in Vitreous Silica: Annealing of the Density Changes[*]

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The kinetics of annealing of the nuclear reactor radiation-induced change in density of a sample of irradiated vitreous silica was studied by means of a series of isothermal annealings performed at various temperatures. The property change was found to anneal gradually over a broad range of temperatures suggesting a range of activation energies for annealing.

INTRODUCTION

A CHANGE in the properties of a vitreous silica sample exposed in a nuclear reactor was found by Primak, Fuchs, and Day.[1] They found that the original properties were restored when the irradiated vitreous silica was heated.[2,3] In these preliminary experiments, the heating was performed at randomly chosen temperatures for arbitrary periods of time, and no attempt was made to study the kinetics. The kinetics of the annealing of nuclear reactor radiation-damaged substances was first investigated by Neubert,[4] who concluded that the data were best explained by assuming that the annealing processes were distributed in activation energy.[5] The theory of the annealing of processes distributed in activation energy was investigated by Vand[6] and was extended by Primak.[7] Such kinetics seems typical of disordered solids, microscopically inhomogeneous but macroscopically homogeneous. It was thought that an excellent example of this kind of kinetics would be found in the annealing of radiation-damaged vitreous silica for it is a disordered solid to begin with. The density was the property chosen for study because it could be determined precisely with the samples available, 40–80 mesh grains of irradiated vitreous silica.

EXPERIMENTAL

Samples

The samples had been prepared by Fuchs and Primak. Commercial vitreous silica was crushed in a steel mortar, graded by sifting, and then washed successively with hydrochloric acid and water. The irradiated sample was exposed in a nuclear reactor for 59 units. (This unit is described by Primak, Fuchs, and Day[3] and Primak,[8] and is approximately 10^{18} neutrons/cm^2 having energies in excess of 10^4 ev.) After irradiation, the grains were found to be coated with a brown organic tar probably formed by the polymerization of traces of organic compounds present in the irradiation can. The tar was removed by treating the grains successively with liquid bromine, alcoholic potash, and chromic acid—sulfuric acid cleaning solution. The grains were then washed successively with water and acetone and dried. Samples used for the annealing studies were individual grains selected for transparency and regular shape under a binocular microscope. Individual grains were transferred to Pyrex glass or vitreous silica capillary flotation tubes (like the ones described by Primak and Day[9] in their Fig. 1*A*) in which they remained throughout the course of density determinations and annealings.

Density Determinations

The densities were determined by the flotation techniques described by Primak and Day.[9] The flotation liquid was a mixture of methylene bromide and

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[*] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[†] Present address: Canisius College, Buffalo, New York.

[1] Primak, Fuchs, and Day, Phys. Rev. **92**, 1064 (1953).

[2] Primak, Fuchs, and Day, Bull. Am. Ceram. Soc. **33**, program p. 25, following p. 130 (1954).

[3] Primak, Fuchs, and Day, J. Am. Ceram. Soc. **38**, No. 4, 135 (1955).

[4] T. J. Neubert (unpublished report, March, 1944); post-deadline paper presented at the American Physical Society Meeting, Baltimore, March 17, 1955 (to be published).

[5] Work done at the Metallurgical Laboratory of the University of Chicago in 1944. (Private communication from M. Burton.)

[6] V. Vand, Proc. Phys. Soc. (London) **55**, 222 (1943).

[7] W. Primak, Phys. Rev. **100**, 1677 (1955).

[8] W. Primak, Phys. Rev. **95**, 837 (1954).

[9] W. Primak and P. Day, Anal. Chem. **26**, 1515 (1954).