computer at the National Bureau of Standards, Boulder, Colorado. My sincerest thanks to General Atomic for granting the leave of absence which made this work possible and to the Joint Institute for Laboratory Astrophysics which, through its very successful visiting fellows program, supported much of this study.

[†] Research supported in part by National Aeronautics and Space Administration Goddard Space Flight Center, under Contract No. NAS 5-9321.

[*] Visiting fellow, the Joint Institute for Laboratory Astrophysics, Boulder, Colorado, 1965-1966.

[‡] Permanent address: General Atomic Division, General Dynamics Corporation, San Diego, California.

[1] G. J. Schulz, Phys. Rev. Letters 13, 583 (1964).

[2] K. Smith, R. P. McEachran, and P. A. Fraser, Phys. Rev. 125, 553 (1962).

[3] P. G. Burke and H. M. Schey, Phys. Rev. 126, 149 (1962).

[4] H. Kleinpoppen and V. Raible, Phys. Letters 18, 24 (1965).

[5] From a discussion with H. Kleinpoppen, I have learned that the angle θ is 94 deg with an uncertainty of ±2 deg and that the maximum value of $\Delta\theta$ is ~10 deg. Nearly all data were collected at the one scattering angle $\theta = 94 \pm 2$ deg.

[6] J. Wm. McGowan, E. M. Clarke, and E. K. Curley, Phys. Rev. Letters 15, 917 (1965); 17, 66(E) (1966).

[7] J. Wm. McGowan, General Atomic Report No. GA-7415 (to be published).

[8] J. Wm. McGowan, M. A. Finemann, E. M. Clarke, and H. P. Hanson, General Atomic Report No. GA-7387 (to be published).

[9] C. Schwartz, Phys. Rev. 124, 1468 (1961).

[10] Since the close-coupling calculations exhibit the resonance in the phase shifts, it was necessary to extrapolate linearly through the resonances to get the background contribution above.

[11] R. P. McEachran and P. A. Fraser, Proc. Phys. Soc. (London) 82, 1038 (1963).

[12] For a review of this material, refer to J. M. Blatt and V. F. Weisskopf, Theoretical Nuclear Physics (John Wiley & Sons, Inc., New York, 1952).

[13] The positions of the resonance are those calculated by T. F. O'Malley and S. Geltman, Phys. Rev. 137, A1344 (1965), and verified by work to be reported (see Ref. 7).

[14] The widths used are experimental, taken from the analysis in Ref. 7.

RAMAN SCATTERING BY LOCAL MODES IN GERMANIUM-RICH SILICON-GERMANIUM ALLOYS

D. W. Feldman, M. Ashkin, and James H. Parker, Jr.
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

(Received 31 October 1966)

We have observed Raman scattering by localized vibrational modes associated with substitutional silicon atoms in the germanium lattice. Silicon and germanium form a mixed crystal in all proportions.[1] Because the silicon mass is much less than that of germanium, one would expect local modes to be associated with the motion of silicon atoms in germanium.[2] Because germanium and silicon have a common valency, such modes are not expected to be infrared active in first order;[3,4] however, they should be Raman active.[5]

The Raman spectra were taken in a spectrometer which is described elsewhere.[6] The spectra were dispersed by two half-meter grating monochromators in tandem and detected by a cooled S-11 photomultiplier. The exciting light was the 4880-Å line of an argon-ion laser and all spectra were taken at 300°K. At the higher concentrations the Raman character of all lines reported has been confirmed by observing them in the anti-Stokes components. The samples consisted of mechanically polished slices. Some of the samples were cut from seed-pulled boules grown at Westinghouse, and others were obtained from the RCA Research Laboratories. Silicon concentrations of all samples were determined by density measurements.[1] Figure 1 shows the Raman spectra obtained from pure germanium,[6] germanium containing 1.5% Si, 8% Si, 25% Si, and pure silicon.[6] In mixed crystals ranging from about 1% to 33% Si, we find a line whose Raman frequency varies with concentration from 389 to 402 cm^{-1}. We identify this line with a local mode associated with an isolated silicon atom. At 5% silicon and above, we observe an additional band at about 462 cm^{-1}. This band consists of two lines whose areas are in the ratio of about 1:2. We tentatively identify it with local modes associated with nearest-neighbor pairs of Si atoms. We note that even at 33% Si, there is no observable line at the pure-silicon value, indicating that there is no appreciable fraction of the silicon present as a separate phase.

We also note that the line in the Raman spec-

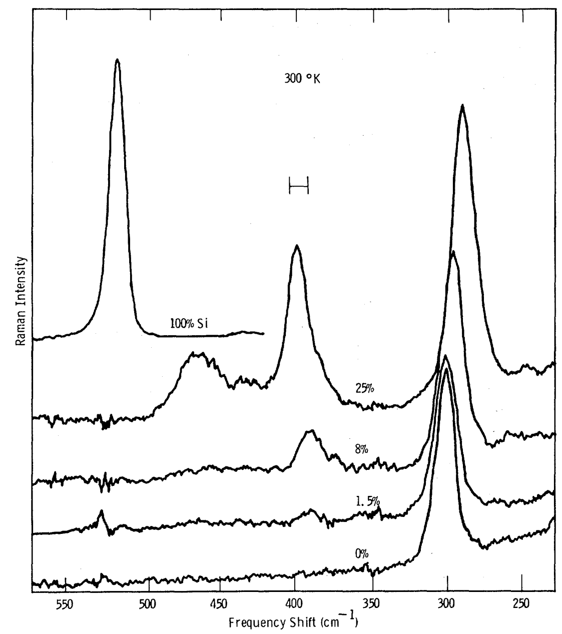

FIG. 1. Raman spectra of germanium-silicon alloys for several compositions. The instrumental resolution is indicated by the vertical lines.

tra of the mixed Si-Ge system which corresponds to the $k \approx 0$ optical mode in pure Ge behaves differently from that observed by Chang, Lacina, and Pershan[7] in the mixed alkaline-earth fluoride system. Rather than shifting upward continuously from the one component's frequency to the other, we observe that the frequency of the Ge mode actually shifts slightly downward with increasing Si content. At 33% silicon this downward shift is about 7% of the germanium-mode frequency.

Xinh[8] has treated Raman scattering of light by crystals of the diamond structure containing substitutional random-mass defects and no force-constant changes. He obtained theoretical expressions for the Raman spectra using a phonon proper self-energy calculated to lowest order in the concentration of the minority atoms.[9] His results should be valid, therefore, only for small concentrations. These results, when applied to silicon in germanium, show that the Raman-active localized mode frequency for small finite concentrations is slightly higher than the localized mode frequency for a single isolated mass defect. The theory also predicts that the peak in the Raman spectra of the disordered crystal which corresponds to the optical mode ($k \approx 0$) of the perfect germanium crystal should shift to lower frequencies. Using a germanium frequency distribution function obtained by Dolling and Cowley,[10,11] the Raman frequency shift of the local mode has been computed for a range of concentrations. These theoretical results are supposedly valid only for small concentrations of silicon; theoretical results for large concentrations of Si are not available.

The experimental data for the local mode frequency ν as a function of silicon concentration c can be represented by

$$\nu = (389 \pm 2) + (0.5 \pm 0.1)c,$$

where ν is in cm^{-1} and c is the concentration in atomic percent. The value of this frequency for $c \lesssim 15\%$ from Xinh's theory is $\nu = 373 \pm 2.6c$. The differences between these two expressions may be attributed in part to the neglect, in the theory, of force-constant changes and anharmonicity or to inaccuracies in the germanium frequency distribution function due to the experimental error in the neutron scattering measurements on which it is based. The Dawber and Elliott[2] theory, using a Debye model, yields 392 cm^{-1} for the frequency of the isolated local mode. In applying this theory, the Debye frequency was set equal to the germanium optical-mode frequency ($k = 0$).

When a pair of defect atoms are substitutionally introduced into an otherwise perfect crystal, under appropriate conditions vibrations of the crystal, localized about the members of the pair, with frequencies outside the vibrational bands of the perfect crystal can occur.[2,12] The theory for these localized modes of a linear chain with nearest-neighbor interactions of germanium masses and containing a pair of silicon-mass defects, illustrates how the frequencies of these modes change with the separation between the members of the pair.[2] For this chain when the silicon atoms are separated by at least two lattice spacings, the difference between the frequencies of the localized pair mode and that of the single-defect localized mode is less than 2% of the single-defect localized-mode frequency, which is less than the observed linewidth of the single-defect local mode. Assuming that this holds for the diamond lattice, only nearest-neighbor site pairs would be expected to give lines outside the single-defect line near 400 cm^{-1}. For Si nearest neighbors in the above linear chain, the frequency of the even mode (symmetric under an inversion about the midpoint of the pair), taking the maximum frequency of the chain as 301 cm^{-1}, is 460 cm^{-1} which is to be compared to the two observed lines at ~448 and ~476 cm^{-1}. The presence of two lines ~448 and 476 cm^{-1} with an intensity ratio 1:2 gives further support to our assumption about the pair nature of this band. The site of a nearest-neighbor Si pair has D_{3d} symmetry and therefore there should be for the mass-defect case three Raman-active localized modes involving motions of the pair, one A_{1g} mode and two degenerate E_g modes.[13] For the mass-defect case these two symmetry types are degenerate. However, when we take into account that the interaction involving two silicons is different from those of the pure germanium lattice,[14] the symmetry argument is unchanged, but the single A_{1g} mode is split from the two degenerate E_g modes.

The assignment of the lines at ~400 and 462 cm^{-1} is partially based on the variation of their intensity with Si concentration. In view of the previous paragraph, only nearest-neighbor site pairs will be considered. Therefore, the peak intensity of the line associated with the pair local mode I_P is proportional to $c^2(1-c)^6$, the probability of having a nearest-neighbor pair surrounded by six nearest-neighbor germanium atoms. This assumes that the crystal is completely disordered. The intensity of the optical mode line I_{Ge} will be assumed to be proportional to $(1-c)^5$, the probability of having a Ge surrounded by four nearest-neighbor Ge. In view of the accuracy of the intensity measurements, this simple picture should suffice. We therefore, have $I_P/I_{\mathrm{Ge}} \propto c^2(1-c)$. In a similar way, $I_L/I_{\mathrm{Ge}} \propto c(1-c)^{-1}$, where I_L is the intensity of the line associated with the single-atom local mode.

To test these assumptions, the measured intensity ratios I_P/I_{Ge} and I_L/I_{Ge} have been fitted to the functions $Ac^2(1-c)$ and $Bc(1-c)^{-1}$, respectively. Figure 2, which shows these measured points and the functions, indicates that the concentration dependence at or below 25% Si is reasonably well described by this simple theory. The occurrence of multiple points at a given concentration indicates the scatter in our measurements.

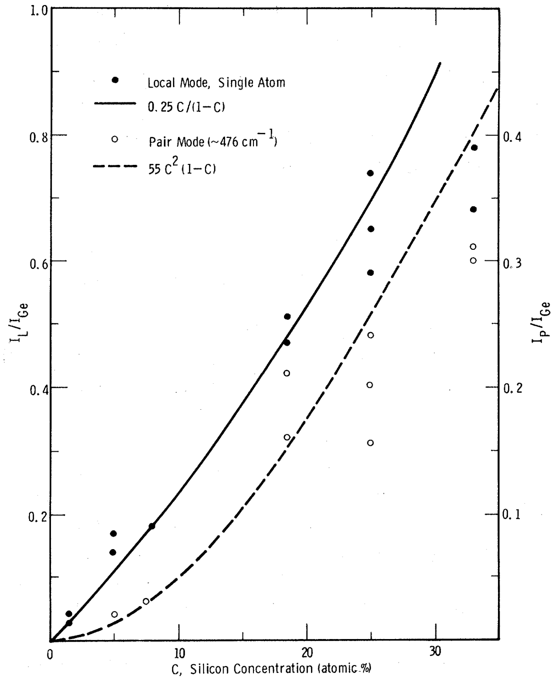

FIG. 2. Ratio of peak intensities of the single-atom local-mode line I_L to the germanium optical-mode line I_{Ge}, and of the pair local-mode line I_P to the germanium line, as a function of silicon concentration. The solid and dashed curves represent best fits to the simple theory discussed in the text.

Previous studies of infrared absorption[15,3] and phonon-assisted electron tunneling[16] properties of Si-Ge alloys have been interpreted in terms of a model involving ordering of the silicon atoms in the germanium lattice, even at very low Si concentrations. If our assumption that only nearest-neighbor atoms need be counted in calculating the intensity of the local modes and optical modes is correct, then our results are more consistent with a random crystal model than with the ordered model proposed by Braunstein, Moore, and Herman.[15] Experimental work is now in progress on Raman studies covering the entire range of this alloy system in order to clarify the random versus ordered model. Calculations also are being performed to obtain the frequencies of different types of isolated pairs for this system.

From our experimental results and in accordance with the above discussion, we conclude that the Raman line at ~400 cm^{-1} for germanium-rich Si-Ge alloys corresponds to a localized mode associated with isolated Si atoms in the germanium lattice, and tentatively assign the observed lines near 462 cm^{-1} to the localized modes of nearest-neighbor pairs of Si atoms. We further conclude that up to 33% Si there is no appreciable precipitation of silicon as a separate phase.

The authors wish to acknowledge helpful discussions with Dr. G. Dolling and to thank him for providing us with detailed numerical values of the germanium frequency distribution function and to thank Dr. B. Abeles and Dr. E. F. Hockings of the RCA Research Laboratories for several alloy samples.

---

[1] J. P. Dismukes, L. Ekstrom, and R. J. Paff, J. Phys. Chem. 68, 3021 (1964).

[2] E. W. Montroll and R. B. Potts, Phys. Rev. 100, 525 (1955); E. W. Montroll and R. B. Potts, Phys. Rev. 102, 72 (1956); P. G. Dawber and R. J. Elliott, Proc. Roy. Soc. (London) A273, 222 (1963).

[3] R. Braunstein, Phys. Rev. 130, 879 (1963).

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

[5] A. A. Maradudin, Rept. Progr. Phys. 28, 331 (1965).

[6] James H. Parker, Jr., D. W. Feldman, and M. Ashkin, Westinghouse Research Laboratories Scientific Paper No. 66-1F6-TPROP-P1, 1966 (unpublished).

[7] R. K. Chang, Brad Lacina, and P. S. Pershan, Phys. Rev. Letters 17, 755 (1966).

[8] N. X. Xinh, Westinghouse Research Laboratories Scientific Paper No. 65-9F5-442-P8, 1965 (unpublished).

[9] A. A. Maradudin, Astrophysics and the Many Body Problem (W. A. Benjamin, Inc., New York, 1963), p. 109.

[10] G. Dolling and R. A. Cowley, Proc. Phys. Soc. (London) 88, 463 (1966); G. Dolling, private communication.

[11] The Ge frequency-distribution function given in Ref. 10 is for 90°K. Following a suggestion of Dolling (private communication) based on the work of B. N. Brockhouse and B. A. Dasannacharya [Solid State Commun. 1, 205 (1963)], the distribution at 300°K was obtained from the one at 90°K by multiplying all vibrational frequencies by 0.983.

[12] J. Hori and T. Asahi, Progr. Theoret. Phys. (Kyoto) 17, 523 (1957); J. S. Langer, J. Math. Phys. 2, 584 (1961); A. A. Maradudin, Westinghouse Research Laboratories Scientific Paper No. 63-129-103-P9, 1963 (unpublished).

[13] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, Molecular Vibrations (McGraw-Hill Book Company, Inc., New York, 1955).

[14] It is probably necessary to also consider changes in the Ge-Si interactions as indicated by the comparison of the experiment and theory for the single-defect local mode. However, the main features of the positions and intensity ratio should be given by the present simple model.

[15] R. Braunstein, A. D. Moore, and F. Herman, Phys. Rev. 109, 695 (1958); R. Braunstein, Phys. Rev. 130, 869 (1963).

[16] R. A. Logan, J. M. Rowell, and F. A. Trumbore, Phys. Rev. 136, A1751 (1964).

SCHOTTKY EMISSION AS A RATE-LIMITING FACTOR IN THERMAL OXIDATION OF METALS*

A. T. Fromhold, Jr., and Earl L. Cook†
Department of Physics, Auburn University, Auburn, Alabama

(Received 29 August 1966)

A new model for the kinetics of thermal oxidation of metals is presented which is based on the hypothesis that the rate-limiting step is thermal excitation of electrons or electron holes over Schottky-type barriers in a diffusion-controlled electric field created by the ionic species.

Wagner[1] based a theory for the formation of coherent oxide (and other tarnish) layers on metals on the hypothesis that particle transport through the layer occurs by the separate diffusion of ions and electrons by lattice-defect mechanisms, the driving force being the electrochemical potential gradient in the layer. The formation rate was considered to be limited by either ions or electrons, depending upon which had the smaller partial conductivity since equal magnitude charge currents were assumed. This model has been verified for a number of tarnishing processes,[1] one example apparently being very thick copper-oxide films (1.25×10^{-2} cm) formed during the high-temperature oxidation of copper.[2] Equal charge concentrations of the oppositely charged diffusing species at every point in the film is a basic assumption for the Wagner parabolic growth law ($L \propto t^{1/2}$) relating film thickness L of the layer to formation time t. An alternative parabolic growth law[3] with a different rate constant has been derived for the case of thinner oxide films (<10 000 Å), where the condition of charge neutrality among species cannot generally be met. The principal assumption in the derivation is that the space-charge concentrations are low enough so that the surface-charge field is the predominant electric field in the film. The situation intermediate to these two extremes is difficult to treat, since the space-charge problem is nonlinear. Although space-charge effects