has been found by Novikova and Shelimova,¹⁴ suggesting a transition at 75°K. Possibly a different stoichiometric composition of their sample is responsible for the difference.

The results for the crystal structure of GeTe.¹² and the measurements of Bierly, Muldawer, and Beckman,¹³ taken in conjunction with our own, make it clear that the transition in GeTe is a displacive transition to a ferroelectric phase, differing from that in certain materials having the perovskite structure only in that the high conductivity prevents any direct measurement of the dielectric constant, and possibly in being a true second-order transition. Correspondingly, SnTe is an example of a "near ferroelectric" having lattice dynamical properties analogous to those of SrTiO₃. One of us (W.C.) had pointed out¹¹ that there is no reason in principle why a diatomic ionic crystal should not have a ferroelectric phase. The extent to which SnTe or GeTe should be regarded as ionic is debatable, especially since they display features in common with the bismuth structure¹⁵ and also have a narrow band gap. These results are also of interest with regard to the suggestion of Anderson and Blount¹⁶ that V_sSi may be a "ferroelectric metal."

We would like to thank Dr. R. S. Allgaier and Dr. B. B. Houston for helpful discussions and for supplying single crystals of SnTe. We are indebted to Professor Barrett for a preprint of his paper. ¹B. N. Brockhouse, in <u>Proceedings of the Symposium</u> on Inelastic Scattering on Neutrons from Solids and <u>Liquids, October 1960</u> (International Atomic Energy Agency, Vienna, 1961).

²W. R. Burke, R. S. Allgaier, B. B. Houston, J. Babiskin, and P. G. Siebenmann, Phys. Rev. Letters <u>14</u>, 360 (1965).

³H. R. Riedl, J. R. Dixon, and R. B. Schoolar, Solid State Commun. <u>3</u>, 323 (1965).

⁴W. Cochran, R. A. Cowley, G. Dolling, and M. M. Elcombe, to be published.

⁵M. M. Elcombe, to be published.

⁶R. A. Cowley and G. Dolling, Phys. Rev. Letters <u>14</u>, 549 (1965).

⁷B. B. Varga, Phys. Rev. <u>1</u>37, A1896 (1965).

⁸R. Lyddane, R. Sachs, and E. Teller, Phys. Rev. <u>59</u>, 673 (1941).

⁹W. Cochran, Phys. Letters 13, 193 (1964).

¹⁰R. A. Cowley, Phys. Rev. Letters <u>9</u>, 159 (1962).

¹¹P. W. Anderson, in Fizika Dielektrikov, edited by

G. I. Skanavi (Akademia Nauk SSSR, Fizicheskii Inst.

im. P. N. Lebedeva, Moscow, 1960); W. Cochran,

Phys. Rev. Letters 3, 412 (1959); Advan. Phys. 9, 387

(1960); R. A. Cowley, Phil. Mag. <u>11</u>, 673 (1965).
¹²J. Goldak, C. S. Barrett, D. Innes, and W. Youdelis,

J. Chem. Phys. <u>44</u>, 3323 (1966). 13 J. N. Bierly, L. Muldawer, and O. Beckman, Acta

Met. <u>11</u>, 447 (1963).

¹⁴S. I. Novikova and L. E. Shelimova, Fiz. Tverd. Tela <u>7</u>, 2544 (1965) [translation: Soviet Phys.-Solid State 7, 2052 (1966)].

¹⁵M. H. Cohen, L. M. Falicov, and S. Golin, IBM J. Res. Develop. 8, 215 (1964).

 16 P. W. Anderson and E. I. Blount, Phys. Rev. Letters 14, 217 (1965).

RAMAN SCATTERING FROM MIXED CRYSTALS $(Ca_x Sr_{1-x})F_2$ AND $(Sr_x Ba_{1-x})F_2^{\dagger}$

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The first-order Raman spectrum of mixed crystals of $Ca_x Sr_{1-x}F_2$ and $Sr_x Ba_{1-x}F_2$ has been measured. The Raman frequency varies linearly with concentration, while the Raman linewidth exhibits a maximum near the 50% mixture.

This paper reports the first application of first-order Raman scattering to the study of lattice dynamics in disordered crystals. The one previous observation of Raman scattering from disordered crystals, mixed crystals of KBr-KCl, employed the second-order Raman effect, and the results were too complex to be readily interpretable.¹ The results reported here on the CaF_2-SrF_2 and SrF_2-BaF_2 systems are for first-order Raman scattering, and the results are readily interpretable. This work was stimulated by the considerable recent interest in the vibronic properties of disordered crystals. Theoretical studies by Poon and Bienenstock,^{2,3} Langer,⁴ Bradley,⁵ Dean,⁶ Maradudin and Weiss,⁷ and Maradudin, Montroll, and Weiss⁸ have obtained details of the elastic vibrational spectrum for various models of mixed crystals. There are no serious discrepancies between these authors. The experimental situation, however, has been far less satisfactory. Braunstein⁹ studied the infrared absorption spectra of mixed Si-Ge crystals. He concluded that the vibronic spectra consisted of modes characteristic of both pure Si and pure Ge. This would have been expected if the mixture did not form a perfect solid solution. On the other hand, other evidence indicated the Si-Ge system was a homogenous solution. Similar results have been found by Verleur and Barker¹⁰ and Chen, Shockley, and Pearson¹¹ on the GaAs_{χ}P_{1- χ} system, by Oswald¹² on InAs_{χ}P_{1- χ}, and by Balkanski, Beserman, and Besson¹³ on CdS_{χ}Se_{1- χ}.

In contrast to this, Logan, Rowell, and Trumbore¹⁴ concluded from their experiments on phonon-assisted electron tunneling with Ge-Si alloys that, for a particular phonon mode, the frequency is a single-valued function of concentration, varying smoothly from the pure Si crystal to the pure Ge crystal. Potter and Stierwatt¹⁵ studied the infrared properties of $GaAs_{\chi}Sb_{1-\chi}$ and, contrary to work mentioned previously, ¹⁰⁻¹³ they found only a single absorption peak whose frequency shifted continuously with increasing *x* from the pure GaSb value to the pure GaAs value. Similarly, Gulisse et al.¹⁶ found the Reststrahlen frequency of $Ni_x Co_{1-x}O$ to be a linear function of concentration. The alkali halides also seem to exhibit this same behavior.¹⁷ The Raman modes studied here also shift linearly with concentration, varying smoothly from one pure crystal to the other.

Balkanski, Beserman, and Besson¹³ attributed the smooth behavior of the <u>Reststrahlen</u> modes in the ionic crystals, in contrast to the different behavior in most of the covalent crystals, as due to long-range electrostatic forces. Although this argument seems reasonable for the <u>Reststrahlen</u> modes with their large electric dipole moments, it is not so convincing for Raman-type modes in the CaF_2 isomorphs, for which there is no electric dipole moment.

Single crystals of $Ca_x Sr_{1-x} F_2$ and $Sr_x Ba_{1-x} F_2$ were obtained from Optovac, Incorporated, for varying values of x. These crystals are known to form continuous solid solutions.^{18,19} This fact is substantiated from our x-ray studies of the crystals used here, which have a lattice parameter linearly dependent on x, in excellent agreement with other published measurements.²⁰ This, by the way, is a very good indication that there is no significant error in the concentration parameter x. For all crystals studied, the x-ray powder pattern only revealed diffraction lines of a fcc lattice. The diffraction lines from the mixed crystals showed no broadening compared with that of the pure crystals. With a signal-to-noise ratio for the x-ray measurement in excess of 100:1, none of the extra diffraction lines of a single cubic lattice appeared. We thus concluded that the crystals used are homogeneous random mixtures with CaF₂ structure.

The pure CaF_2 , SrF_2 , and BaF_2 crystals have, in first order, a single allowed Raman-active mode in which the cation remains stationary and the F⁻ ions vibrate against each other. We observe that the mixed crystals also have only one observable Raman-active mode and, as shown in Fig. 1, the frequency of that mode is a linear function of composition, varying smoothly from pure crystal (with x = 0) to pure crystal (with x = 1).

In view of the fact that the wave vector \vec{k} is not a good quantum number for the random crystal, one might expect to observe Raman



FIG. 1. The first-order Raman frequency of mixed crystals $Ca_x Sr_{1-x} F_2$ and $Sr_x Ba_{1-x} F_2$ as a function of the concentration x. In all these crystals, there is only one first-order Raman vibration.



FIG. 2. A typical Raman spectrum of the [40% Ca, 60% Sr]F₂ crystal in which we searched for additional lines. Note that there is but one Raman peak and this is between that of pure CaF₂ and pure SrF₂ (indicated by arrows). Data are obtained from a multichannel analyzer.

scattering from other vibrational modes. Figure 2 shows a typical Raman spectrum [40% Ca, 60% Sr] in which we searched for additional lines. Actually, we searched over a wider wavelength range than displayed and Fig. 2 is simply intended to illustrate the typical sensitivity. With this sensitivity, no additional lines were seen, although we were able to detect the 408-cm⁻¹, second-order line, in pure CaF₂. This line is off the scale of Fig. 2.

Aside from the linear shift of frequency with composition, the only other effect of disorder was an increased linewidth for the Raman lines. This is shown in Fig. 3 for scattering at room temperature. The instrumental width (i.e., laser width, spectrometer slit width, etc.) is approximately 5 cm⁻¹. The Raman lines are broadest at about 50% composition, and if one subtracts the instrumental width, the Raman linewidth is from three to four lines broader than in the pure crystals. These widths are all temperature dependent, and further measurements are being made to separate the effects of temperature from the effects of disorder. Typically the lines narrow by about a factor of 3-4 in going from room temperature to 77°K.

Qualitatively, one would expect the linewidths in the mixed crystals to be greater than in the pure crystals since the elimination of the translational symmetry leads to the breakdown of the $\vec{k} = 0$ selection rule. Quantitatively, however, there is no good theory for the variation of linewidth with concentration. Qualitatively, the linear variation of Raman frequency with concentration could also be explained by simply assuming the so-called "virtual-crystal" approximation. Poon and Bienenstock² discuss this approximation in which all masses are taken as average masses and all spring constants are the average spring constant for the two-dimensional lattice with one atom per primitive cell. In their model, which has only acoustic modes, they can justify the virtual-



FIG. 3. The total linewidth measured at half-intensity of the first-order Raman-scattered light from the mixed crystals $Ca_x Sr_{1-x} F_2$ at room temperature. The instrumental linewidth is 4.7 cm⁻¹.

crystal approximation to first order in the wave vector \vec{k} . Although they find that the spring constant for the virtual crystal is really obtained by averaging the reciprocal spring constants, this difference would be unimportant for the measurements shown in Fig. 1, since the force constants to be averaged are only slightly different. It is not at all obvious, however, that their results apply for the optical modes to which this, and other, experimental data are related. There remains a need for more theoretical work on this problem.

In view of the seemingly contradicting results on other systems, $^{9-15}$ the CaF₂-SrF₂ and SrF₂- BaF_2 solid solutions represent a rather clear experimental result. Firstly, the x-ray and Raman data, taken together, absolutely demonstrate the crystals are both homogeneous and random solid solutions. In general this is a rather difficult thing to establish. Secondly, for the Raman mode in CaF_2 and its isomorphs], the Ca++ ion does not move. Theoretically, this problem can thus be treated as one in which the "spring constants" change but the masses are left invariant. This is not the case for most of the other studies on mixed crystals, the one exception possibly being the NiO-CoO solution. On the other hand, that system has long-range electric dipole forces. This leads to the third advantage of studying the Raman mode in CaF₂ solutions rather than the infrared-active Reststrahlen modes, namely the absence of the complicating dipolar forces.

In view of the simple behavior of the center frequency of the Raman mode as a function of concentration, it should be possible to explain the temperature and concentration dependence of the Raman linewidth. This would be an excellent test for any detailed theory of lattice vibrations in disordered crystals. Although the second-order Raman spectrum of pure CaF_2 is not yet well understood,²¹ it should eventually be possible to study the second-order Raman spectra of these mixed crystals and thus obtain information on the effects of disorder on other phonon modes.

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¹A. I. Stekhanov and M. B. Éliashberg, Opt. i Spektroskopiya <u>10</u>, 348 (1961) [translation: Opt. Spectr. (USSR) <u>10</u>, 174 (1961)]; Fiz. Tverd. Tela <u>2</u>, 2354 (1960) [translation: Soviet Phys.-Solid State <u>2</u>, 2096 (1961)].

²Hin-Chiu Poon and Arthur Bienenstock, Phys. Rev. <u>142</u>, 466 (1966).

³Hin-Chiu Poon and Arthur Bienenstock, Phys. Rev. <u>141</u>, 710 (1966).

⁴J. S. Langer, J. Math. Phys. <u>2</u>, 584 (1961).

⁵J. C. Bradley, Ann. Phys. (N. Y.) <u>15</u>, 411 (1961).

⁶P. Dean, Proc. Roy. Soc. (London) <u>A254</u>, 507 (1960).

⁷Alex Maradudin and George H. Weiss, J. Soc. Ind. Appl. Math. <u>6</u>, 302 (1958).

⁸A. A. Maradudin, E. W. Montroll, and G. H. Weiss, <u>Theory of Lattice Dynamics in the Harmonic Approxi</u>

mation (Academic Press, Inc., New York, 1963). 9 R. Braunstein, Phys. Rev. <u>130</u>, 879 (1963).

¹⁰H. W. Verleur and A. S. Barker, Jr., Phys. Rev. <u>149</u>, 715 (1966).

¹¹Y. S. Chen, W. Shockley, and G. L. Pearson, Phys. Rev., to be published.

¹²F. Oswald, Z. Naturforsch. <u>14A</u>, 374 (1959).

¹³M. Balkanski, R. Beserman, and J. M. Besson, Solid State Commun. <u>4</u>, 201 (1966).

¹⁴R. A. Logan, J. M. Rowell, and F. A. Trumbore, Phys. Rev. 136, A1751 (1964).

¹⁵R. F. Potter and D. L. Stierwatt, in <u>Proceedings</u> of the International Conference on Physics of Semi-

conductors, Paris, 1964 (Dunod, Paris, 1964), p. 1111. ¹⁶P. J. Gulisse, J. N. Pendl, L. C. Mansar, R. Mar-

shall, and S. S. Mitra, J. Appl. Phys. <u>36</u>, 2447 (1965).

¹⁷R. M. Fuller, C. M. Randall, and D. J. Montgomery, Bull. Am. Phys. Soc. <u>9</u>, 644 (1964).

¹⁸E. Rumpf, Z. Physik. Chem. (Leipzig) <u>B7</u>, 148 (1930).

¹⁹E. Beck, Metallurgie <u>5</u>, 514 (1908).

²⁰E. G. Chernevskaya and G. V. Anan'eva, Fiz. Tverd.

Tela <u>8</u>, 216 (1966) [translation: Soviet Phys.-Solid State <u>8</u>, 169 (1966)].

 $^{21}A.$ R. Gee, D. C. O'Shea, and H. Z. Cummins, Solid State Commun. $\underline{4}$, 43 (1965).