citation energies to account qualitatively for the low-temperature variation of the specific heat in liquid He^3.

We are very grateful to J. R. Schrieffer for letting us have a copy of his work before publication and for interesting correspondence, and to D. F. Brewer for helpful conversations. S. Engelsberg would like to thank the physics department of Imperial College for their kind hospitality during the summer of 1966.

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DIATOMIC FERROELECTRICS

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Experimental measurements of the phonon dispersion relation for SnTe suggest that the phase transition of GeTe and SnTe/GeTe alloys is of a displacive character, similar to that of the perovskite ferroelectrics. They therefore provide the first examples both of diatomic ferroelectrics and of "ferroelectric semiconductors," with a narrow band gap.

These measurements are part of a program to study the phonon dispersion relations of diatomic crystals having high dielectric constants by means of the method of inelastic neutron scattering.[1] SnTe has the sodium chloride structure, and as-grown crystals are slightly nonstoichiometric with a relatively high-carrier concentration[2] which prevents any direct measurement of the static dielectric constant, $\epsilon(0)$. The value of the high-frequency dielectric constant is $\epsilon(\infty) = 42 \pm 4$.[3]

Figure 1 shows the phonon frequencies $\nu_j(\vec{q})$ for the optic branches, for wave vectors in the [001] direction, at a number of temperatures. The transverse optic (TO) branch is very temperature dependent, in contrast to the weak temperature dependence of the other [001] branches of the dispersion relation. Figure 2 shows the square of the frequency of the TO mode at small wave vector $\vec{q}$, as a function of temperature. The bars indicate uncertainty mainly due to the difficulty of correcting these particular measurements for the effect of the finite resolution of the triple-axis spectrometer.

It is evident from Fig. 1 that as $\vec{q}$ approaches zero the frequency of the longitudinal optic (LO) mode falls sharply. A similar effect has been found in PbTe[4] and in PbS,[5] although it is much less marked in these materials. This effect can be understood in terms of the screening of the LO mode by carriers in the conduc-

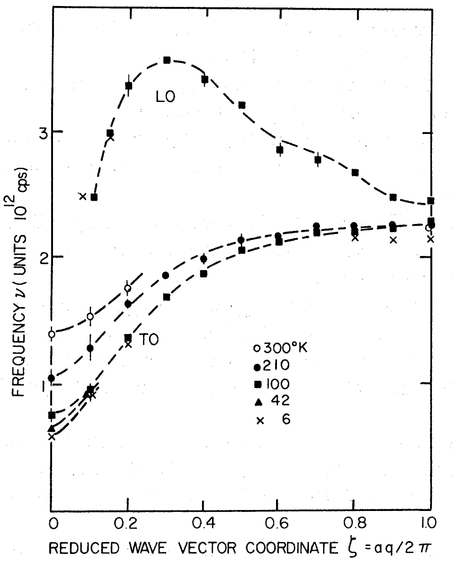

FIG. 1. The dispersion relations for the optic normal modes of vibration propagating along the [001] direction in SnTe at various temperatures.

tion band, using the theories of Cowley and Dolling[6] and of Varga,[7] and we are not primarily concerned with it here. The value of $\nu_{LO}(q \rightarrow 0)$ after an estimated allowance for this effect is $(4.2 \pm 0.2) \times 10^{12}$ cps. Application of the Lyddane-Sachs-Teller relation[8] then gives $\epsilon(0) = 1200 \pm 200$ at 100°K.

We believe the shape of the TO branch of the dispersion curves to be an intrinsic property of SnTe. It is qualitatively similar to that of PbTe, although for this material the temperature dependence of $\nu_{TO}(q \rightarrow 0)$ is comparatively small.[9] Both the shape of the curve for SnTe and its temperature dependence resemble those of a TO mode of $SrTiO_3$, although in the latter material the variation of the squared frequency is more nearly linear with temperature.[10] However, since a linear temperature dependence is a high-temperature approximation, it is to be expected that deviations may occur at low temperatures. The relation of this mode to the dielectric properties of a material has been discussed by several authors,[11] and it is generally accepted that the temperature variation shown in Fig. 2 foreshadows a transition to a ferroelectric phase. Evidently the cubic structure remains just stable at 0°K for our specimen of SnTe.

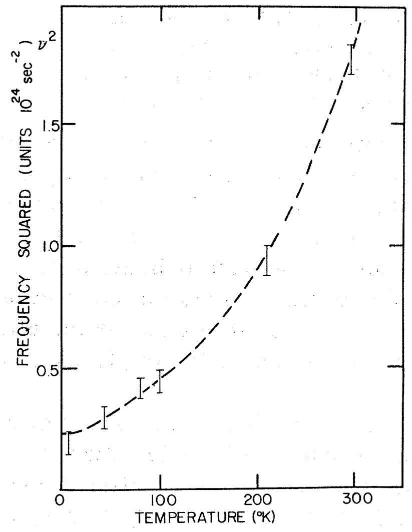

FIG. 2. The square of the frequency of the transverse optic mode of vibration of very long wavelength as a function of temperature for SnTe.

It is however known that GeTe, which has the sodium chloride structure above about 670°K, has a trigonally distorted acentric structure below this temperature.[12] That these two structures are related by a ferroelectric type of transition can be seen by considering the atomic coordinates. If we take the origin of coordinates as midway between the Na and Cl ions in the NaCl structure, the ions are on face-centered lattices with origins at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and $(-\frac{1}{4}, -\frac{1}{4}, -\frac{1}{4})$, respectively. The distorted structure can be obtained by displacing the lattices to (u, u, u) and $(-u, -u, -u)$, with $u = 0.237$, and then expanding the lattice along the [111] direction to make the interaxial angle 88.2° at 300°K.[12] Clearly the former distortion can be obtained from a transverse optic mode of long wavelength displacement along a [111] direction, which destroys the center of symmetry of the structure and results in polarization appearing along the [111] direction. The latter distortion then arises from an expansion of the crystal along the ferroelectric axis. In $BaTiO_3$ the relative displacement of the ions in the transition is also accompanied with an expansion of the crystal along the ferroelectric axis. Furthermore, SnTe and GeTe form a continuous range of solid solutions, the transition temperature of which varies almost linearly with composition. Extrapolation of the results published by Bierly, Muldawer, and Beckman[13] would indicate a transition temperature for SnTe in the neighborhood of 0°K, which is not inconsistent with our observations.

An anomaly in the thermal expansion of SnTe 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 $\mathrm{SrTiO_3}$. One of us (W.C.) had pointed out[11] 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 structure[15] and also have a narrow band gap. These results are also of interest with regard to the suggestion of Anderson and Blount[16] that $\mathrm{V_3Si}$ may be a "ferroelectric metal."

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RAMAN SCATTERING FROM MIXED CRYSTALS $(\mathrm{Ca}_x\mathrm{Sr}_{1-x})\mathrm{F}_2$ AND $(\mathrm{Sr}_x\mathrm{Ba}_{1-x})\mathrm{F}_2$†

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The first-order Raman spectrum of mixed crystals of $\mathrm{Ca}_x\mathrm{Sr}_{1-x}\mathrm{F}_2$ and $\mathrm{Sr}_x\mathrm{Ba}_{1-x}\mathrm{F}_2$ 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 $\mathrm{CaF_2}$-$\mathrm{SrF_2}$ and $\mathrm{SrF_2}$-$\mathrm{BaF_2}$ 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 Weiss[8] 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. Braunstein[9] studied the in-