

### Vibrations of a One-Dimensional Ionic Lattice

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The singularities in the distribution of vibrational frequencies in the one-dimensional ionic lattice are studied. It is shown that presence of Coulomb forces, however weak, not only produces at least one additional singularity, but also changes the nature of one singularity qualitatively.

THE vibrational spectra of infinite one-dimensional crystals have been studied for many years.<sup>1,2</sup> Results cannot be applied to real crystals directly, but are often obtained in closed form by mathematically simple methods. Certain conclusions can thus be drawn in a particularly clear-cut way and extended to real crystals later. On the other hand, direct calculations in more than one dimensions of models with long-range (Coulomb) forces have had to rely mostly on numerical methods.<sup>3</sup> More recently it has been shown that the frequency distribution of any crystal will exhibit certain singularities<sup>4</sup>; and since these singularities constitute the most striking feature of the distributions, attention has been drawn to the problem of locating them and studying their nature. The purpose of this note is therefore to investigate the singularities in the frequency distribution of the one-dimensional lattice with Coulomb forces. It turns out that when all atomic masses are equal, the presence of Coulomb forces produces a new singularity regardless of how slight the Coulomb forces may be compared to the short-range forces, and that the nature of one of the singularities is changed qualitatively, differing from the usual inverse-square-root behavior. When atoms of opposite charge have different mass (as in case of all real ionic crystals) the allowed frequencies separate into two bands and additional singularities appear, as is usual; but again the behavior of only one of them differs from the usual inverse-square-root one.

Consider, then, an infinite chain of atoms a distance *a* apart. Let atoms *i* and *i'* interact by the usual Coulomb force  $(-)^{i+i'}e^2/r_{ii'}^2$  and in addition let nearest neighbors interact with Hooke's law force constant  $\alpha$ . At first, for simplicity, let all atoms have the same mass *m*. Then Newton's equation of motion for the displacement *u<sub>i</sub>* of the *i*th atom,

$$m\ddot{u}_i = F_i^{\text{short}} + F_i^{\text{Coulomb}}$$

can be solved by expanding  $F^{\text{Coulomb}}$  in terms of the *u<sub>i</sub>* and making the usual normal mode transformation

$$u_i = U \exp[i(\omega t + i\pi p)].$$

<sup>1</sup> M. Born and Th. von Kármán, *Physik. Z.* **13**, 297 (1912); M. Blackman, *Proc. Roy. Soc. (London)* **A148**, 365 (1935).

<sup>2</sup> E. Broch, *Proc. Cambridge Phil. Soc.* **33**, 485 (1937).

<sup>3</sup> M. Smollett, *Proc. Phys. Soc. (London)* **A65**, 109 (1952); E. W. Kellerman, *Trans. Roy. Soc. (London)* **238**, 513 (1940); M. Iona, *Phys. Rev.* **60**, 822 (1941); H. B. Rosenstock, *J. Phys. Chem. Solids* **4**, 201 (1958).

<sup>4</sup> L. van Hove, *Phys. Rev.* **89**, 1189 (1953).

We find

$$\lambda(p) = \lambda_0(p) - \sigma S(p), \tag{1}$$

where we have defined  $\lambda = m\omega^2/2\alpha$ ,  $\sigma = 2e^2/\alpha a^3$ , and where

$$\lambda_0(p) = 1 - \cos p \tag{2}$$

is the well-known expression for the squared frequency of a one-dimensional metal and

$$S(p) = \sum_{k=1}^{\infty} (-)^k k^{-8} [\cos(k\pi p) - 1]. \tag{3}$$

$S(p)$  is best studied with the use of two series,<sup>5</sup> of which at least one converges rapidly for any value of *p* of physical interest ( $0 \leq p \leq 1$ ):

$$S(p) = \sum_{n=0}^{\infty} c_{2n} p^{2n+2} \quad \text{for } 0 \leq p < 1, \tag{4}$$

or

$$S(p) = 2\xi_3 + T(q) \quad \text{for } 0 \leq q < 2,$$

with

$$T(q) = \sum_{n=0}^{\infty} \gamma_{2n} q^{2n+2},$$

where

$$q = 1 - p, \quad c_{2n} = -\pi^2 \xi_{2n} / n(2n+1)(2n+2),$$

and

$$\gamma_{2n} = c_{2n} / (2^{2n} - 1),$$

for

$$n \geq 1, \quad c_0 = \frac{1}{2}\pi^2 \ln 2, \quad \gamma_0 = \frac{1}{2}\pi^2 (\ln \pi q - \frac{3}{2}),$$

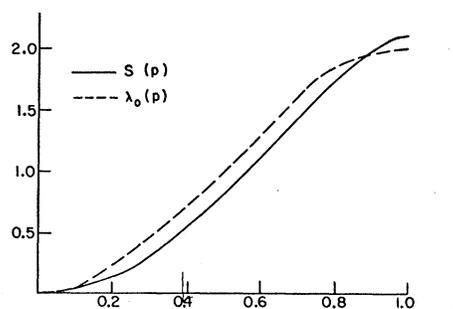


FIG. 1. The functions  $\lambda_0$  and  $S$  as defined by (2) and (3).

<sup>5</sup> H. B. Dwight, *Tables of Integrals* (The Macmillan Company, New York, 1947), formulas 630.1, 630.2, and 47.3.

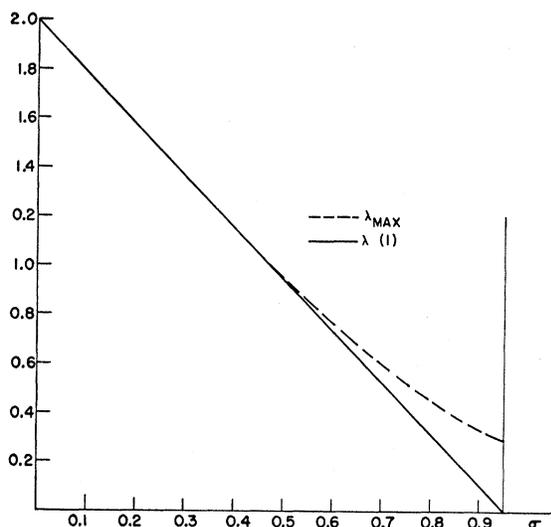


FIG. 2. Critical points of  $\lambda(p)$  as a function of  $\sigma$ .

and the

$$\xi_n = \sum_{h=0}^{\infty} (2h+1)^{-n},$$

are known constants.<sup>6</sup> Both  $S(p)$  and  $\lambda_0(p)$  are shown in Fig. 1, and  $\lambda(p)$  as given by (1) can be constructed from them for any  $0 \leq \sigma < \xi_3^{-1} = 0.9508$  [for larger  $\sigma$ ,  $\lambda(1)$  becomes negative which implies that the lattice is unstable].

In the metallic case  $\sigma=0$ ,  $\lambda(p)$  is known to have only two critical points, a minimum at  $p=0$  and a maximum at  $p=1$ . In the ionic case, the interesting modification

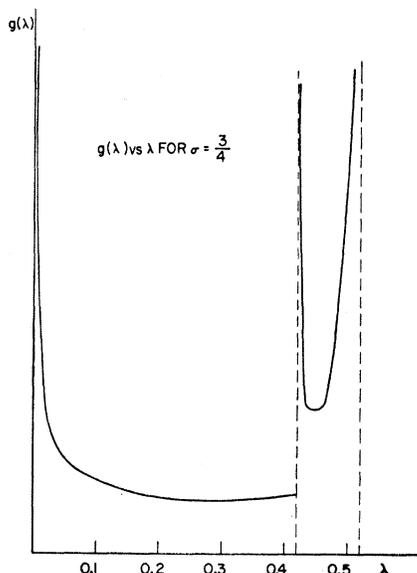


FIG. 3. Frequency distribution,  $\sigma = \frac{3}{4}$  (ordinate scale arbitrary).

<sup>6</sup> T. J. Stieltjes, *Acta Mathematica* **10**, 299 (1887).

results from the second term,  $-\text{const } q^2 \ln q$ , in the expansion of  $\lambda(p)$  about  $\lambda(1)$ . In the first place, it differs from the usual  $\text{const } q^2$ ; also, since it is positive the point  $p=1$  is a minimum rather than a maximum; and an ordinary maximum,  $\lambda_{\text{max}}$  will appear elsewhere (at a point we shall call  $p_{\text{max}}$ ) between  $p=0$  and  $p=1$ . In addition, there is always the usual minimum at  $p=0$ . The values of the two critical points  $\lambda_{\text{max}}$  and  $\lambda(1)$  as a function of  $\sigma$  are shown in Fig. 2.

The function of interest in physical problems is the frequency distribution  $g(\lambda)$ , which in one dimension is equal to  $d\rho/d\lambda$ , and in particular its singularities.<sup>4,7</sup> Their position and nature, for all positive  $\sigma$ , however small, can be deduced from the critical points of  $\lambda(p)$ : there are three of them, at  $\lambda=0$ ,  $\lambda_{\text{max}}$  and  $\lambda(1) = 2(1-\sigma\xi_3)$ . The first two are the usual one-sided infinite peaks of inverse-square-root nature, but the one at  $\lambda(1)$  may be expected to differ from this behavior, though only slightly (in some sense), since  $q^2 \ln q$  differs only "slightly" from  $q^2$ . This statement can be made precise by proving the following theorem:

$$2^{-\frac{1}{2}}\pi[\lambda-\lambda(1)]^{-\frac{1}{2}}(1+\epsilon)[\lambda-\lambda(1)]^{\epsilon/2} < g(\lambda) < 2^{-\frac{1}{2}}\pi[\lambda-\lambda(1)]^{-\frac{1}{2}}$$

holds for all  $\lambda-\lambda(1) < \delta(\epsilon)$ , where  $\delta = (\pi^2/2)(\rho^*)^4$  and  $\rho^*(\epsilon)$  is the solution of  $\rho \exp(\rho^{-4\epsilon/(1+\epsilon)}) = 1$ . Figure 3 shows  $g(\lambda)$  for  $\sigma = \frac{3}{4}$ , a value which is physically reasonable (e.g.,  $0.5 \lesssim \sigma \lesssim 0.8$  for alkali halides of the sodium chloride structure).  $\lambda(1) \rightarrow \lambda_{\text{max}}$  as  $\sigma \rightarrow 0$  and when  $\sigma=0$  (metallic case) they coalesce, leaving only the two well-known inverse-square-root singularities.

If we assume different masses,  $m_1$  and  $m_2 > m_1$ , for adjacent atoms, and write  $\lambda = (m_2 m_1)^{\frac{1}{2}} \omega^2 / 2\alpha$ ,  $r^2 = m_2 / m_1$ , then two values of  $\lambda$  are possible for every  $0 \leq p \leq 1$  and two additional singularities of the usual one-sided inverse-square-root type appear in the frequency distribution, at  $\lambda_{\pm}(1/2) = r^{\pm 1}(1 - \frac{3}{4}\sigma\xi_3)$ . The allowed frequencies appear in two bands, separated by a gap bounded by these two new singularities. There is only one singularity whose behavior differs from the usual one in the described way; this one appears at  $\lambda_+(0) = \lambda_+(1) = (r+r^{-1})(1-\sigma\xi_3)$ .

It has been known for sometime that introduction of new forces into the crystal models often increases the complexity of and in particular the number of singularities in the frequency distribution,<sup>8</sup> and the appearance of more singularities on account of Coulomb forces should therefore occasion no surprise. What is of interest however are the following two facts: first, a new singularity occurs however small the Coulomb forces may be; second, the new singularity that occurs is of a qualitatively different kind from the usual inverse-square-root singularity. Since the nature of the singularities themselves differ with dimensionality, precise

<sup>7</sup> G. Placzek and L. van Hove, *Phys. Rev.* **93**, 1207 (1954); H. B. Rosenstock, *J. Chem. Phys.* **27**, 1194 (1957).

<sup>8</sup> H. B. Rosenstock, *Phys. Rev.* **97**, 290 (1955); J. C. Phillips, *Phys. Rev.* **104**, 1263 (1956).

conclusions directly applicable to phenomena in three-dimensional crystals<sup>7</sup> cannot be drawn at this time. It does not seem possible to extend these calculations to two or three dimensions by the use of the present, or similarly simple, methods: we have been unable to generalize the simple representation (4) of the lattice sum (3) to higher dimensions. Representations, obtained by the use of theta functions, do exist<sup>9</sup> and pro-

<sup>9</sup> M. Born and M. Bradburn, Proc. Cambridge Phil. Soc. **39**, 104 (1942).

vide a good starting point for numerical work; but they do not provide one with a comparably simple expansion of the dispersion relation about the critical points which are required for an investigation of the resulting singularities. Although one may conclude from these representations that the behavior of the dispersion relation will differ from the usual quadratic one, we have been unable to determine the precise effect on the frequency distribution from them. A detailed investigation of these "unusual" singularities in three dimensions would be of considerable significance.

## Thermoelectric Power of Dilute Indium-Lead and Indium-Thallium Alloys\*†

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An earlier investigation of the thermoelectric power of dilute ( $\alpha$ -phase) indium-lead alloys, measured relative to pure indium, indicated that there is detailed structure superimposed on the smooth trend of the data. This investigation is now extended to include some twenty-two indium-lead alloys as well as thirteen indium-thallium alloys. For the indium-lead alloys, the existence of structure at both 273°K and 77°K is reaffirmed. On the other hand, the thermoelectric power of the indium-thallium system is found to be an extremely smooth function of the composition in the same range of solute concentration. As a consequence, it is concluded that the observed structure in indium-lead is due exclusively to changes in electronic concentration brought about by alloying.

An estimate of the pure electronic concentration contribution to the thermoelectric power is obtained by subtracting the indium-thallium data from the corresponding indium-lead data. The results of this procedure are demonstrated to be in qualitative agreement with the predictions of a band-model theory which is developed for this comparison. It is therefore suggested that the observed structure can be attributed to the extinction of bands of electron holes and the initiation of bands of overlap electrons. Furthermore, as the result of comparing the thermoelectric data with lattice spacing information, definite suggestions are made concerning the band configuration of pure indium and the evolution of said configuration with alloying. Finally, a very qualitative explanation is offered for the novel face-centered tetragonal ( $c/a > 1$ ) to face-centered tetragonal ( $c/a < 1$ ) phase transformation which occurs at the  $\alpha$ -phase solubility limit.

### I. INTRODUCTION

**I**n general, the addition of a solute impurity differing in valence from the solvent metal produces three important changes relative to conditions existing in the pure solvent: the concentration of nonlocalized electrons changes, thereby changing the Fermi-level; the coupling of such electrons to the lattice changes because of increased impurity scattering, thereby changing the electronic relaxation times; and the strains introduced by the addition of foreign ion-cores cause a relaxation of the Fermi-surface. (This last effect will be assumed quite small by comparison and consequently ignored. In the future, the remaining two effects will be referred

to as the electronic concentration effect and the lattice effect, respectively.)

Recent work on the composition dependence of the thermoelectric power of dilute magnesium alloys, as measured relative to pure magnesium, indicates that the lattice and electronic concentration effects may be separated by considering the two contributions to be algebraically additive.<sup>1</sup> Thus, for example, the electronic concentration contribution for a magnesium-indium alloy of a given atomic percent composition is obtained by subtracting the observed thermoelectric power of a magnesium-cadmium alloy of identical atomic composition from the observed value for the magnesium-indium alloy. According to this scheme, the thermoelectric power of the magnesium-cadmium alloy system represents, to some degree of approximation, the lattice contribution associated with the solutes of the fifth period of the periodic table.

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<sup>1</sup> Salkovitz, Schindler, and Kammer, Phys. Rev. **105**, 887 (1957).