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Phonon Assignments in ZnSe and GaSb and Some Regularities in the Phonon Frequencies of Zincblende-Type Semiconductors*

S. S. MITRA
Physics Research Division, IIT Research Institute†, Chicago, Illinois

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The lattice infrared-absorption spectra of ZnSe and GaSb reported in the literature are analyzed to obtain the values of the optical and the acoustical phonon energies at or near the Brillouin zone boundary. For ZnSe, which has an effective ionic charge of 0.7, the LO and TO phonons are found to have about the same energy near the zone boundary as anticipated by Keyes for compounds of intermediate ionicity. Mass ratio and effective ionic-charge effects in the critical-point phonon energies of the zincblende-type semiconductors are investigated with the presently available data. The difference in the values of the longitudinal and the transverse optical modes at the zone center is found to be a linear function of ionicity. If the observed infrared spectra of these compounds are analyzed on a four-phonon scheme, new correlations are obtained between the optical and the acoustical phonon energies. These correlations are discussed in terms of dispersion relations.

I. INTRODUCTION

THE infrared-absorption spectrum of a diatomic ionic cubic crystal like NaCl or ZnS is expected, from elementary theory, to consist of a single line associated with the optical lattice mode of essentially zero propagation vector. For diatomic homopolar crystals like diamond or silicon, this lattice fundamental should be a single line active in the Raman scattering only. However, the infrared absorption spectra of both ionic and homopolar crystals are known to consist of a number of secondary maxima in the high-energy side of the fundamental, originating from multiple phonon combinations.

For polar crystals, the mechanism of interaction of electromagnetic field with phonons causing the side bands has been explained[1] as due to the anharmonic part of the potential energy associated with the lattice vibrations. For homopolar crystals, Lax and Burstein[2] have shown that two or more phonons can interact directly with the radiation through terms in the electric moment of second or higher order in the atomic displacements. The interactions of either origin are governed by the conservation of energy and the wave vector. Strictly speaking, the combinations should give rise to continuous absorption. Absorption maxima, however, occur because of singularities in the phonon frequency distribution. Such singularities occur where the dispersion curves for the individual branches are flat, which is the case at or near the edge of the Brillouin zone. A given phonon branch can thus be characterized by a single frequency. The broadening of combination bands is explained as due to strong dependence of the energy on the wave-vector direction at the Brillouin zone boundary.

In recent years, a considerable amount of interest has been shown in the study of lattice infrared absorption spectra of diamond- and zincblende-type crystals. The transverse optical mode in silicon, corresponding to the zone center lattice fundamental is infrared inactive. However, ten peaks were reported[3] in the lattice absorption. These were interpreted as two- and three-phonon combination bands by using four characteristic phonon energies. Similar studies have also been made for diamond,[4] Ge,[5] and SiC.[6] Among the III–V semiconductors, optical lattice absorption spectra have been investigated for GaP,[7] InSb,[8] and GaAs.[9] The most comprehensive study of this type was reported[10] for AlSb. The reststrahlen band of this compound occurs at 31.5μ. However, 35 absorption maxima have been observed as far down as 9.3μ, resulting from multiphonon combinations involving as many as four phonons. The factor group active lattice fundamental in InP occurs at 32μ. Newman[11] has observed absorption bands in the region 15.2 to 26.4μ. Hilsum and Rose-Innes[12] have tentatively assigned these bands to the multiphonon combinations. Harmon, Genco, Allred, and Goering[13] have reported more structure in the region 10 to 14μ. Hrostowski and Fuller[14] have observed

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structure in the lattice absorption spectrum of GaSb but no assignments have been made.

The infrared lattice spectra of a number of zincblende-type II–VI semiconductors have been reported either in reflection or in absorption. Multiple-phonon structure, however, has been observed only in ZnS [15] and ZnSe,[16] with no phonon assignments for the latter.

The purpose of the present communication is to interpret the reported infrared absorption maxima in ZnSe and GaSb as multiple-phonon combinations and to point out some regularities in the phonon energies of the zincblende-type crystals.

II. COMBINATION BAND ASSIGNMENT FOR ZnSe

The lattice infrared spectrum of ZnSe has been measured by Aven, Marple, and Segall.[16] The strongest lattice absorption occurs at 0.026 eV, and is obtained from an analysis of the reststrahlen spectrum. This band is identified with the transverse optical phonons at or near the Brillouin zone center. Six additional absorption bands were also recorded at higher energies, but no assignments were given. These are identified with two and three phonon processes. Assuming two optical and two acoustical phonon frequencies at or near the zone boundary given by 212, 208, 162, and 87 cm^{-1}, respectively, all the observed bands can be explained. The assignments are shown in Table I. It will be noted that the values of the two optical phonons near the zone boundary are very nearly the same. In fact, a satisfactory set of calculated combination frequencies can be obtained with only three characteristic phonon frequencies (one optical and two acoustical). A qualitative explanation of this degeneracy will be offered in Sec. IV. It may suffice here to say that for certain intermediate values of the effective ionic charge (q^*) the zone-boundary values for the two optical branches tend to coincide, as they do at the zone center for $q^*=0$ (e.g., Si). The effective ionic charge for ZnSe as calculated from the reststrahlen spectrum by the Szigeti relation[17] is 0.7, and, as will be evident later, falls in the range of intermediate ionicity by our definition. A nearly similar situation exists for GaP.

TABLE I. Two- and three-phonon combination bands in ZnSe as calculated from the four characteristic phonon frequencies LO = 208 cm^{-1}, TO = 212 cm^{-1}, LA = 162 cm^{-1}, and TA = 87 cm^{-1}.

Peak position[a] in eV	Peak position[a] in cm^{-1}	Assignment	Calculated position in cm^{-1}
0.031	250	LA+TA	249
0.037	298	LO+TA TO+TA	297
0.046	371	LO+LA TO+LA	372
0.052	420	LO+TO	420
0.062	501	2LO+TA	503
0.073	588	2TO+LA	586

[a] Data Ref. 16.

The Brout-Blackman[18] sum rule has been recently applied to GaP, AlSb, and GaAs. By assuming Coulomb attractive forces and nearest-neighbor repulsive forces, Brout[19] has obtained the following relation:

$$\sum_{i=1}^{6}\omega_i(\mathbf{k})^2=\left(\frac{1}{M_+}+\frac{1}{M_-}\right)\frac{18r_0}{\chi}, \qquad (1)$$

where χ is the compressibility, M_+ and M_- are the ionic masses, r_0 the nearest-neighbor distance, and $\hbar\omega_i(\mathbf{k})$ is the phonon energy of the ith vibrational branch at wave vector $\mathbf{k}$. The zincblende-type crystals are not expected to follow this relation precisely. However, when the sum is evaluated for phonon energies corresponding to $\mathbf{k}=0$ and some $\mathbf{k}$ at or near the edge of the Brillouin zone in the cases of GaP [7] and AlSb,[10] the values obtained for each agreed within 8%. However, for GaAs the phonon assignment made by Spitzer[20] showed only a poor agreement (~20%).

The transverse optical phonon for ZnSe at $\mathbf{k}=0$ has an energy of 0.026 eV (210 cm^{-1}). The longitudinal phonon frequency is 250 cm^{-1}. It is calculated from the above value by the Lyddane-Sachs-Teller[21] formula:

$$\omega_l/\omega_t=(\epsilon_0/\epsilon_\infty)^{1/2}, \qquad (2)$$

where ϵ_0 and ϵ_∞ correspond to low- and high-frequency dielectric constants. Therefore,

$$\sum_{i=1}^{6}\omega_i(\mathbf{k}=0)^2=2\omega_t^2+\omega_l^2=0.536\times10^{28}\ \text{sec}^{-2}. \qquad (3)$$

From the frequencies LO, TO, LA, and TA of Table I, the value of this sum for some $\mathbf{k}$ at or near the zone boundary is

$$2(\text{TO})^2+(\text{LO})^2+2(\text{TA})^2+(\text{LA})^2 =0.580\times10^{28}\ \text{sec}^{-2}. \qquad (4)$$

The agreement between the Brout sums for the zone center and the zone edge phonons of ZnSe is thus fairly satisfactory. In Eqs. (3) and (4) the factor of 2 arises from the assumed degeneracy of the transverse modes.

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III. COMBINATION BAND ASSIGNMENT FOR GaSb

The reststrahlen spectrum of GaSb has been investigated by Picus, Burstein, and Henvis[22] and by Hass and Henvis.[23] These studies made with rather impure samples gave values of the zone center transverse optical mode at 231 cm^{-1}, and an effective ionic charge of 0.33. However, owing to high free-charge-carrier absorption, combination lattice bands could not be observed by transmission measurements. By supersaturating compensation of impure *p*-type GaSb crystals with Li at high temperatures, Hrostowski and Fuller[14] were able to reduce the free-charge-carrier absorption to a point where it was possible to record the complete infrared lattice spectrum in transmission. They reported absorption maxima at 19.8, 23.3, 24.4, 28.5, 30.7, 34.5, 40, and 41μ. No assignment of these bands, however, was attempted.

It is highly unlikely that any of these bands are due to ion-pair vibrations. Such bands are expected to be much less intense and to occur at longer wavelengths. The bands observed must belong to the lattice and identified with multiphonon combination bands. With the assumed zone boundary characteristic phonon frequencies of 215 cm^{-1} (TO), 193 cm^{-1} (LO), 134 cm^{-1} (LA), and 49 cm^{-1} (TA), all the absorption bands could be explained as two-, three-, or four-phonon processes. The assignment is shown in Table II. The frequency of the zone-center longitudinal optical mode as calculated from the Lyddane-Sachs-Teller formula is 240 cm^{-1}. The zone-center Brout sum is therefore given by

$$2\omega_t^2+\omega_l^2=0.582\times10^{28}\ \mathrm{sec}^{-2}. \tag{5}$$

The Brout sum at or near the zone boundary using the phonon energies obtained from our assignment is

$$2(\mathrm{TO})^2+(\mathrm{LO})^2+2(\mathrm{TA})^2+(\mathrm{LA})^2 =0.535\times10^{28}\ \mathrm{sec}^{-2}, \tag{6}$$

in reasonable agreement with the value at the zone center.

TABLE II. Multiphonon combination bands in GaSb as calculated from the four characteristics phonon frequencies: LO = 193 cm^{-1}, TO = 215 cm^{-1}, LA = 134 cm^{-1}, and TA = 49 cm^{-1}.

Peak position[a] in eV	Peak position[a] in cm^{-1}	Assignments	Calculated position in cm^{-1}
0.0302	244	LO+TA	242
0.0310	250	2LO−LA	252
0.0359	290	LO+2TA	291
0.0404	326	LO+LA	327
0.0434	350	TO+LA	349
0.0508	410	TO+LO	408
0.0532	429	2TO	430
0.0625	504	TO+LO+2TA	506

[a] Data Ref. 14.

IV. TRENDS IN THE CHARACTERISTIC PHONON FREQUENCIES OF THE ZINCBLENDE-TYPE CRYSTALS

As already pointed out, the multiple structure observed in the lattice infrared spectra of the zincblende-type crystals can usually be accounted for in terms of four characteristic phonon energies belonging to the four branches: transverse acoustic, longitudinal acoustic, longitudinal optical, and the transverse optical at the Brillouin zone boundary. In certain cases, however, some doubts exist concerning the identification of the optical branch phonons as transverse and longitudinal modes. No such difficulty exists for the acoustical branches where the transverse frequency is smaller than the longitudinal one, for all values of the propagation vector (**k**), except at the zone center where both are zero. Keyes[24] has noted some correlation between the zone-boundary phonon energies of the zincblende-type crystals with the mass ratio of their constituent atoms and their ionicity (q^*). The latter correlation enables one to assign the higher two optical phonon frequencies to definite longitudinal and transverse branches.

For homopolar crystals like Si ($q^*=0$), the optical branches are degenerate at the zone center. However, the transverse optical phonons have higher energies than the longitudinal ones at or near the zone boundary. For crystals of low ionicity, the longitudinal optical mode is at a higher frequency compared to the transverse mode (Lyddane-Sachs-Teller's rule) at the zone center. But near the zone boundary the situation is reversed with the transverse modes having higher values than the longitudinal optical modes, as is the case with InSb, GaAs, and GaSb. In the case of GaP and AlSb, however, the LO and TO assignments of Keyes are just the reverse of those of Kleinman and

TABLE III. Zone-center phonon frequencies and effective ionic charge of zincblende-type semiconductors.

Semiconductor	q^*	ν_t (cm^{-1})	ν_l (cm^{-1})	$(\nu_l-\nu_t)/\nu_t$
Si[a]	0	510	510	0
GaSb[b]	0.33	231	240	0.039
InSb[b]	0.42	185	197	0.065
AlSb[c]	0.48	318	345	0.085
GaAs[b]	0.51	273	297	0.088
GaP[d]	0.58	366	402	0.098
InAs[b]	0.58	219	244	0.114
InP[b]	0.68	307	351	0.143
ZnSe[e]	0.7	210	250	0.190
CdTe[f]	0.7	140	169	0.207
ZnS[g]	0.88	312	390	0.250
SiC[h]	0.94	793	970	0.223
ZnO[i]	0.96	387	484	0.250

[a] See Ref. 25.
[b] See Ref. 23.
[c] See Ref. 10.
[d] See Ref. 7.
[e] See Ref. 16.
[f] See Ref. 26.
[g] See Ref. 15.
[h] See Ref. 27.
[i] See Ref. 28.

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TABLE IV. Phonon frequencies obtained from the infrared active combination bands of zincblende-type semiconductors.

Semiconductor	Reference	LO (cm^{-1})	TO (cm^{-1})	LA (cm^{-1})	TA (cm^{-1})	q^{*2}	$\sigma = M_1/M_2$
Si	3	413	482	333	139	0	1.00
SiC	6	851	770	540	363	0.88	2.33
GaP	7	361	378	197	115	0.34	2.25
InP(a)	12	316	341	126	63	0.46	3.70
InP(b)	This study	318	329	150	62	...	...
AlSb	10	298	316	132	65	0.23	4.52
GaAs	9	234	258	188	70	0.26	1.075
GaSb	This study	193	215	134	49	0.11	1.74
InSb	8	155	179	118	43	0.18	1.061
ZnS	15	379	297	263	228	0.77	2.03
ZnSe	This study	208	212	162	87	0.49	1.21

Spitzer[7] and Turner and Reese.[10] The LO phonons have higher energy than the TO phonons at the zone boundary, as well as at the zone center, for crystals of large effective ionic charge like SiC. Figure 1 shows the effect of ionicity on the dispersion curves as discussed above. Keyes has also predicted that the frequencies of the optical branches at the zone boundary coincide for a crystal with effective ionic charge $q^* = 0.7$, which value we term as intermediate. It is indeed the case, as has been noted above, with ZnSe.

The zone-center phonon energies for thirteen zincblende-type crystals are collected in Table III,[25–28] along with their effective ionic charge. It is evident from Fig. 1 that the separation between the LO and TO frequencies at the zone center increases with increasing ionicity. In Fig. 2 is shown a linear plot between $(\nu_l - \nu_t)/\nu_t$ and q^*. The II–VI compounds seem to fall on a different straight line than that for the III–V compounds.

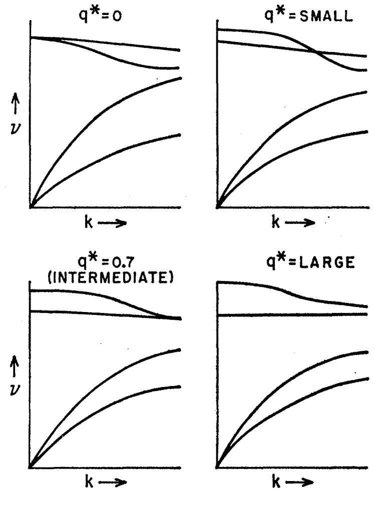

FIG. 1. The effect of ionicity on the dispersion curves.

In Table IV the phonon energies at or near the zone boundary of ten zincblende-type semiconductors are listed along with q^{*2} and $\sigma = M_1/M_2$, the ratio of the larger to the smaller atomic masses. The LO and TO designations are interchanged, whenever necessary, in accordance with Keyes assignments. A plot of $(LO/TO)^2$ versus q^{*2} is shown in Fig. 3. The strong correlation, in spite of wide variation in q^* values reported in the

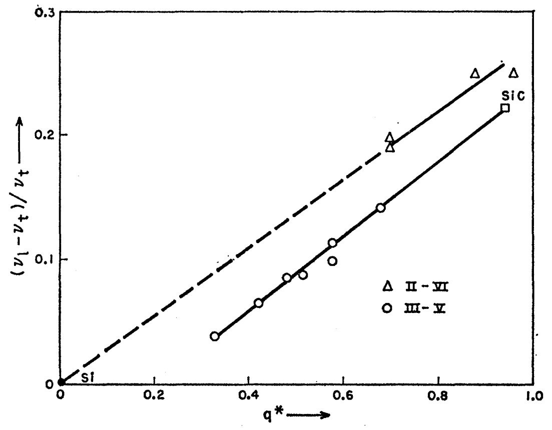

FIG. 2. The effect of ionicity on the separation between the optical longitudinal and transverse modes at the center of the Brillouin zone.

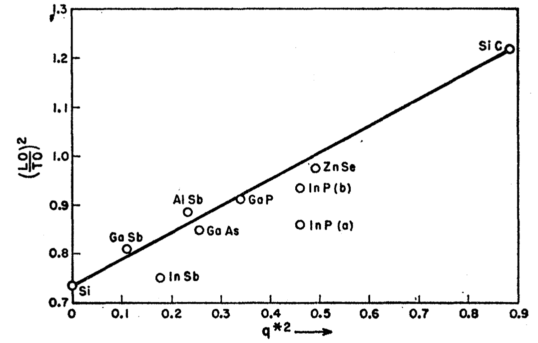

FIG. 3. Dependence of the ratio of the optical frequencies near the zone boundary on the effective ionic charge.

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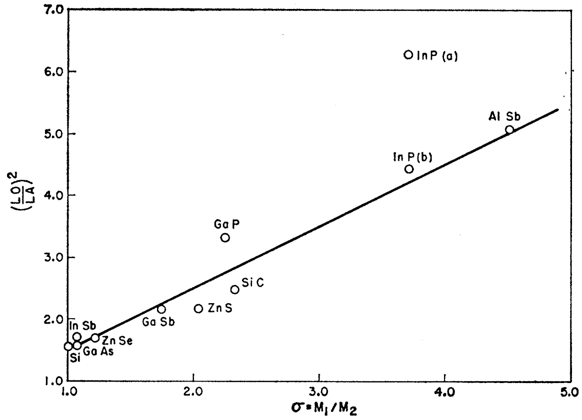

FIG. 4. The effect of mass difference on the separation between the optical and the acoustical branches.

literature, forms the basis of Fig. 1, which is also qualitatively evident from theory.[29]

The theory of a linear diatomic chain[30] suggests that the separation between the optical and acoustical branches at the zone boundary should increase with increasing mass ratio. The $(LO/LA)^2$ versus σ plot of Fig. 4 shows that the same is qualitatively true for the zincblende-type crystals. Keyes[31] has also suggested that a linear relation may be obtained between the separation of longitudinal and transverse acoustical modes at the zone boundary and the ionicity; more specifically $(TA/LA)^2$ and q^{*2}. The data of Table IV, however, do not show a good correlation of this nature. Several other correlations, as expected qualitatively from the dispersion relations of Fig. 1, are possible among the zone boundary phonon energies. Two such, viz., between LO and TA and between TO and LA are shown in Figs. 5 and 6.

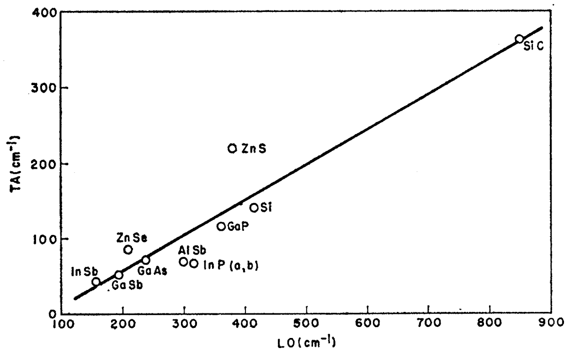

FIG. 5. TA versus LO in the zincblende-type semiconductors.

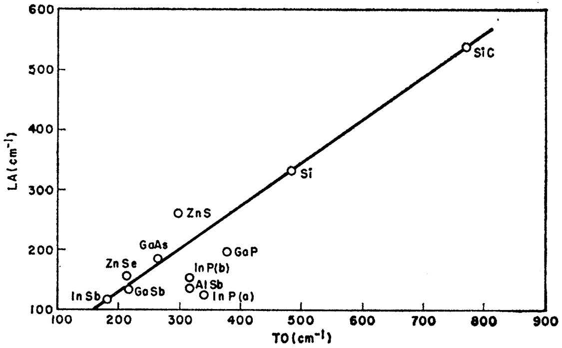

Fig. 6. LA versus TO in the zincblende-type semiconductors.

V. DISCUSSION

Our assignment of ZnSe and GaSb presented earlier seems reasonably correct. Besides explaining the observed infrared transmission spectra, they have also fared well in all the correlations presented above. An interesting point to note is that ZnSe with an ionicity of 0.7 indeed forms an intermediate case, where the transverse and longitudinal optical phonons at the zone boundary have nearly the same energy. The assignments of Tables I and II are tentative. High-resolution spectra of thicker samples at room and lower temperatures are needed before more reliable assignments can be furnished.

In Figs. 3–6, InP deviates badly from the curves. The assignment of the LO, TO, LA, and TA frequencies for this material have been made by Hilsum and Rose-Innes[12] using Newman's[11] data. In our correlations, the LO and TO phonons were interchanged for reasons given by Keyes.[24] In spite of this, the crystal does not follow the correlations well. Deutsch[32] and Spitzer[20] have shown that several sets of phonon assignments are possible in the cases of CdS and GaAs crystals. The same is true for InP, for which another assignment explaining the observed infrared spectrum, as well as obeying most of the above correlations within reasonable limits, could be given. One such assignment is indicated in Table IV and the points due to them are shown as InP(b) in Figs. 3 to 6. The LO and TA assignments remain essentially the same. For TO and LA phonons we have, respectively, assumed values of 329 cm^{-1} and 150 cm^{-1}. The observed[11] bands at 379, 403, 442, 467, 633, and 658 cm^{-1} are explained as LO+TA, LO+LA−TA, LO+2TA, LO+LA, 2LO, and 2TO, respectively.

ZnS is another crystal deserving comment. A perusal of Table IV reveals that the acoustical phonon energies as assigned by Deutsch[15] are unusually large. This is also reflected in Figs. 5 and 6. The Brout sum at the zone center amounts to 1.233×10^{28} sec^{-2} as compared with a value of 1.754×10^{28} sec^{-2} near the zone boundary.

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This large difference (45%) is quite unexpected for a highly ionic crystal like ZnS and is attributed to high values of LA and TA phonons. The discrepancy is even larger if one uses the dielectric constants given by Deutsch[15] instead of those[28,33] used in the calculation of the zone center longitudinal mode. The discrepancy is also larger if one uses the ν_t given by Mitsuishi, Yoshinaga, and Fuyita.[34] A new assignment for ZnS with lower values of LA and TA phonons will, therefore, be in order.

ACKNOWLEDGMENTS

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Theory of High-Temperature Magnetostriction

HERBERT B. CALLEN*
Department of Physics and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania

AND

EARL R. CALLEN
U. S. Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland

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In contrast to the rapid decrease predicted by conventional theory, the magnetostriction λ_{100} of iron has a large maximum just below the Curie temperature. We propose a mechanism based on the fact that an ellipticity in the quasiparticle spectrum permits a lowering of the free energy by distortion; an equivalent mechanism arises from the anisotropic magnon-phonon interaction near the zone boundary. This latter interaction is large at temperatures such that magnon renormalization (due to magnon-magnon interaction) lowers the magnon spectrum to degeneracy with phonons at the zone edge. The degeneracy temperature agrees well with the temperature of the λ_{100} maximum in iron. Adding silicon raises impurity states from the phonon spectrum and thence lowers the degeneracy temperature, but increases the range of temperature over which near-degeneracy occurs; this agrees with the observed shift and broadening of the λ_{100} peak. The mechanism also predicts a monotonically decreasing λ_{111} of the opposite sign to λ_{100}, as observed in iron.

I. INTRODUCTION

THE conventional magnetoelastic coupling theory of magnetostriction[1,2] and the observations of Takaki,[3] Tatsumoto and Okamoto,[4] and Gersdorf[5] on iron are in puzzling disagreement. The magnetoelastic coupling theory predicts that the magnetostriction of ferromagnets should fall monotonically to zero with increasing temperature. In contrast, the magnetostriction constant λ_{100} of iron, shown in Fig. 1(a), increases with increasing temperature, exhibiting a large maximum just below the Curie temperature. Addition of small fractions of silicon shifts the major maximum to lower temperature and broadens it. The second magnetostriction constant λ_{111}, shown in Fig. 1(b), falls monotonically to zero. Finally, the peak in λ_{100} is absent in nickel.

In addition, Tatsumoto and Okamoto[4] report a minor maximum at about one-fifth the Curie temperature (although in private communication they have observed that in this temperature region their data is less reliable because of magnetoresistance in the strain gages). The minor maximum is also suggested by the measurements of Takaki,[3] but is not indicated by the data of Gersdorf.[5]

In this paper we propose a mechanism which accounts qualitatively for the magnitude and location of the high-temperature maximum of λ_{100} in iron, for the shift and broadening of the maximum with the addition of silicon, for the absence or smallness of the effect in nickel, and provides criteria for the presence of the effect in other materials. Furthermore, the theory properly predicts the monotonic behavior of λ_{111} and the fact that λ_{111} and λ_{100} are of opposite sign.

The mechanism depends on the existence of an asymmetry in the excitation spectrum of the system, this

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