Crystal Dynamics of Gallium Arsenide

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The dispersion relation for the normal modes of vibration propagating along the $[\zeta00]$, $[\zeta\zeta\zeta]$, and $[0\zeta\zeta]$ directions in a single crystal of pure gallium arsenide at 296°K has been determined by neutron spectrometry. The frequencies (units 10^{12} cps) of specific modes are (a) (0,0,0): TP 8.02±0.08, LO 8.55±0.20; (b) (1,0,0): TO 7.56±0.08, TA 2.36±0.015, LO 7.22±0.15, LA 6.80±0.06; (c) (0.5,0.5,0.5): TO 7.84±0.12, TA 1.86±0.02, LO 7.15±0.07, LA 6.26±0.10. The results are analysed in terms of the dipole approximation model. Although a fairly complex version of this model provides a satisfactory description of most of the data, certain significant discrepancies remain. These indicate that the neglect of quadrupole interactions is a serious weakness of the dipole approximation model.

IN this paper we present a preliminary report of measurements of the dispersion relationship, $\nu(\mathbf{q})$, for the normal modes of vibration in pure gallium arsenide (GaAs) at 296°K, obtained by means of the coherent one-phonon scattering of slow neutrons[1] from a single crystal specimen. These results, together with the known elastic,[2] dielectric[3] and piezoelectric[4] constants of GaAs, have been analyzed in terms of the so-called dipole approximation (D.A.) model,[5-9] which has recently received considerable theoretical attention as a means of interpreting and correlating the above properties of many crystals having the zinc blende structure. Our analysis indicates the existence of a basic deficiency in the D.A. model. A possible origin of this deficiency is suggested.

The measurements of $\nu(\mathbf{q})$ for GaAs were made using the triple axis crystal spectrometer[10] at the NRU reactor, Chalk River. The frequencies of some normal modes are listed in Table I, and the complete results are illustrated in Fig. 1. The frequencies were determined to within 1%–2%. The longitudinal and transverse optic mode frequencies for zero wave vector, ν_{LO} and ν_{TO}, obey the relation[11]

$$\nu_{LO}/\nu_{TO} = (\epsilon_0/\epsilon_\infty)^{1/2},$$

to well within the experimental uncertainty (ϵ_0, ϵ_∞ are the static and high frequency dielectric constants, respectively). Our values for these frequencies are in fairly good agreement with those deduced from infrared absorption[12] and reflection[13] measurements, and from tunnel diode experiments.[14] The dispersion curves are generally similar, except for the absence of certain degeneracies, to those for germanium[15] and silicon.[6]

TABLE I. Frequencies of some selected modes in gallium arsenide at 296°K.

Mode (wave vector)		Frequency (10^{12} cps)
TO	(0,0,0)	8.02±0.08
LO	(0,0,0)	8.55±0.2
TO	(1,0,0)	7.56±0.08
TA	(1,0,0)	2.36±0.015
LO	(1,0,0)	7.22±0.15
LA	(1,0,0)	6.80±0.06
TO	(0.5,0.5,0.5)	7.84±0.12
TA	(0.5,0.5,0.5)	1.86±0.02
LO	(0.5,0.5,0.5)	7.15±0.07
LA	(0.5,0.5,0.5)	6.26±0.10
IO	(0,0.7,0.7)	7.90±0.15
IIO	(0,0.7,0.7)	6.44±0.12
TO	(0,0.7,0.7)	7.51±0.12
IA	(0,0.7,0.7)	3.48±0.06
IIA	(0,0.7,0.7)	5.65±0.12
TA	(0,0.7,0.7)	2.38±0.04

The mathematical treatment underlying the D.A. model was first proposed by Mashkevitch and Tolpygo[16] and extensively developed by Cochran[5] (We refer the reader to the latter paper for a description of the basic ideas and approximations of the D.A. model.) For the present purpose, it is sufficient to state that the D.A.

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[1] G. Placzek and L. Van Hove, Phys. Rev. 93, 1207 (1954).
[2] T. E. Bateman, H. J. McSkimin, and J. M. Whelan, J. Appl. Phys. 30, 544 (1959).
[3] K. G. Hambleton, C. Hilsum, and B. R. Holeman, Proc. Phys. Soc. (London) 77, 1147 (1961).
[4] The value +3.6×10⁴ esu/cm² (for the piezoelectric constant) is quoted without error in Ref. 9.
[5] W. Cochran, Proc. Roy. Soc. (London) A253, 260 (1959).
[6] G. Dolling, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna 1962), Vol. II, p. 37; also Chalk River Report AECL-1573, 1962 (unpublished).
[7] R. A. Cowley, Proc. Roy. Soc. (London) A268, 121 (1962).
[8] Z. A. Demidenko, T. I. Kucher, and K. B. Tolpygo, Fiz. Tverd. Tela 3, 2482 (1961) [translation: Soviet Phys.—Solid State 3, 1803 (1962)].
[9] H. Kaplan and J. J. Sullivan, Phys. Rev. 130, 120 (1963).
[10] B. N. Brockhouse, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961), p. 113; also Chalk River Report AECL-1183, 1961 (unpublished).
[11] R. H. Lyddane, R. G. Sachs, and E. Teller, Phys. Rev. 59, 673 (1941).

[12] W. Cochran, S. J. Fray, F. A. Johnson, J. E. Quarrington, and N. Williams, J. Appl. Phys. 32, 2102 (1961).
[13] M. Hass and B. W. Henvis, J. Phys. Chem. Solids 23, 1099 (1962).
[14] R. W. Hall and J. H. Racette, J. Appl. Phys. 32, 2078 (1961).
[15] B. N. Brockhouse and P. K. Iyengar, Phys. Rev. 111, 747 (1958).
[16] V. S. Mashkevitch and K. B. Tolpygo, Zh. Eksperim. i Teor. Fiz. 32, 520 (1957) [translation: Soviet Phys.—JETP 5, 435 (1957)].

FIG. 1. Dispersion curves for gallium arsenide based on measurements at 296°K. The solid points denote undetermined polarization. The vertical dashed line in the [0ζζ] direction represents the zone boundary. In this direction, points labeled I, II refer to modes whose polarization vectors are parallel to the (0Ī1) mirror plane. Other modes are either strictly longitudinal (L) or transverse (T). The dotted and solid curves represent calculations based on two modifications, B and C, of the dipole approximation model.
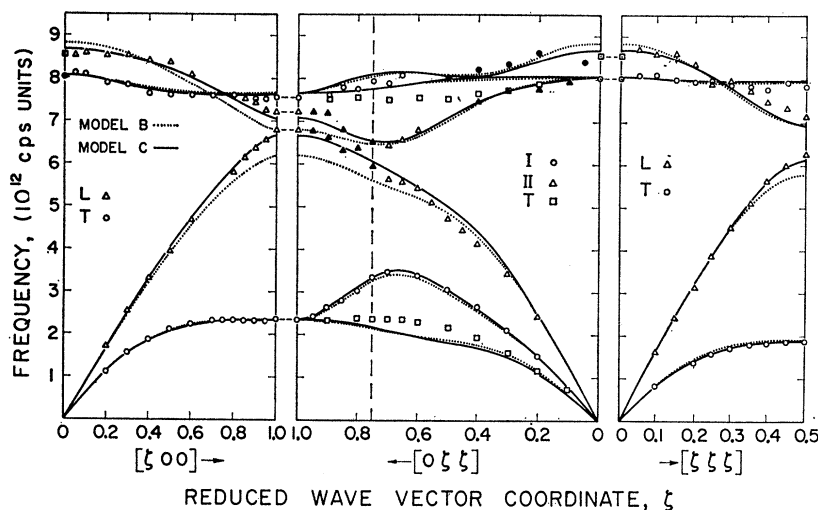
model attempts to take into account the *polarizability* of the atoms in a crystal, and employs short-range force constants between near-neighbor atoms to represent the effects of "overlap" interaction. The distortion of the electronic configuration which occurs during a lattice vibration is represented by an electric multipole expansion which is cut off after the dipole term. It has been found previously[6,8,9,12] that quite adequate agreement between theory and experiment can be achieved by the use of both first and second nearest-neighbor short-range interactions. This is due partly to lack of data, particularly for the III–V semiconductors, and partly to the extreme flexibility (i.e., a large number of disposable parameters are available) of the "second neighbor" D.A. model.

We have analyzed, using a nonlinear least-squares fitting technique, the experimental results for GaAs in terms of a variety of D.A. models, constructed by making various simplifying assumptions to reduce the number of parameters. The results for the two best models, labeled B and C, which have 12 and 14 parameters, respectively, are shown in Fig. 1. Both models include parameters representing second nearest neighbor short-range forces (poor agreement with experiment is obtained without such parameters) and both lead to the assignment of a rather small positive charge (about $0.04e$, $e = 4.803 \times 10^{-10}$ esu) to the Ga atom. The difference between these models can be simply expressed in the notation of Ref. 5. In model B, the parameters γ_R, γ_T and γ_S (which are ratios of first neighbor short-range force constants) are assumed equal. This assumption is consistent with the simple "shell-model" picture of Ref. 5, in terms of which it seems plausible that these γ parameters should be of order unity. For model B, we find the quite reasonable value, $\gamma_R \approx +0.45$. This restriction of equal γ parameters has been relaxed in model C, with the result that γ_R, γ_T and γ_S adopt the very different, and somewhat unlikely (but not impossible) values 0.22,

0.02, −0.20, respectively, while the other 11 parameters remain roughly constant. It is clear from Fig. 1 that a substantially improved fit to the longitudinal modes near the zone boundary in the 3 directions is given by model C. In the [ζζζ] L modes, the atoms adopt configurations extremely suggestive of electric quadrupoles; it seems probable that neglect of specific quadrupole interactions is a serious weakness of the D.A. model, but that the effect of this weakness can be compensated by the adoption of unrealistic values for certain parameters.

The strictly transverse modes in the [0ζζ] direction, with polarization vectors perpendicular to the (0Ī1) mirror planes, were not studied experimentally until after the model analyses had been carried out, and so these results provide an excellent independent check on the force models. We note that even the best model (C) provides a rather poor description of these data. It was a noticeable feature of earlier applications of the D.A. model to germanium and silicon[6] that the complexity of the model required to fit the experimental data increased in proportion to the quantity and quality of those data. We regard the poor fit shown by models B and C to the [0ζζ] T branches in GaAs as a serious failure of this type of D.A. model. It is, of course, possible that these results could be included in future least-squares analyses, and that better agreement might be achieved with force models no more complex than C.

One of the difficulties of the "second neighbor" D. A. models is the practical necessity of reducing the large number of disposable parameters mentioned earlier. An alternative approach to this problem, either by an appeal to a different physical picture of the D. A. model, or better, by a quantum-mechanical calculation of certain force constants from first principles, would be very valuable. We suggest, in the meantime, that the inclusion of specific quadrupole forces in a simple manner, would be more profitable than further

elaboration of the D. A. model. Such models have been proposed by Lax[17] and by Cowley,[7] but both appear to involve a considerable number of disposable parameters, and the problem of parameter determination still remains.

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[17] M. Lax, Phys. Rev. Letters **1**, 133 (1958); and Bull. Am. Phys. Soc. **4**, 181 (1959).

Statistical Mechanics of Dilute Copper Manganese*†

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The low-temperature specific heat and magnetic susceptibility for dilute concentrations of manganese in copper are studied, using the "statistical model" of Margenau and an expansion of the partition function in a power series of the concentration. An indirect "Ising model" interaction via the conduction electrons is assumed to exist between the magnetic impurities. To find a correction to the statistical model, the two-particle correlation function between impurities is derived in the limit as the temperature approaches zero. It is shown that, in this limit, the system is composed of small clusters of spins that are strongly correlated to each other within a cluster, but various clusters are randomly oriented relative to each other. An impurity within one of these clusters finds itself in an "effective field" arising from the other spins within the cluster and from the random orientation of all spins outside the cluster. This field is a random variable and its probability distribution is easily obtained from the model. The detailed shape of the probability distribution of the field is given for a particular concentration. As the temperature is increased, the internal structure of the clusters is broken up and, at high temperatures, the system exhibits paramagnetic behavior. The theory predicts correctly the experimental low-temperature specific heat and magnetic susceptibility of dilute Cu–Mn.

INTRODUCTION

R ECENT experimental studies on dilute concentrations of manganese in copper have revealed several interesting and unusual phenomena. Measurements of the magnetization as a function of temperature[1-4] have shown a maximum in the low-temperature magnetic susceptibility. This maximum occurs at a temperature approximately proportional to the impurity concentrations and is found at 13 and 40°K for a 1.4 and 5.6 at.% Mn, respectively. The existence of

the susceptibility maximum was interpreted[1] to be a gradual transition to antiferromagnetism as the temperature is lowered; others[5] suggested that the system may be composed of small ferromagnetic domains aligned antiferromagnetically. The high-temperature paramagnetic susceptibility obeys the Curie-Weiss law with positive temperature intercept characteristic of a ferromagnetic interaction and indicates that the magnetic moment of Mn is close to 5 Bohr magnetons. The system also exhibits remarkable low-temperature specific heat anomalies. Measurements by Zimmerman and Hoare[6,7] have shown that the alloys exhibit a large excess specific heat compared with that of pure copper, the excess being independent of the Mn concentration and increasing linearly with temperature. To explain

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[1] J. Owen, M. Browne, W. D. Knight, and C. Kittel, Phys. Rev. **102**, 1501 (1956).

[2] J. Owen, M. Browne, V. Arp, and A. F. Kip, J. Phys. Chem. Solids **2**, 85 (1957).

[3] I. S. Jacobs and R. W. Schmitt, Phys. Rev. **113**, 459 (1959).

[4] R. W. Schmitt and I. S. Jacobs, J. Phys. Chem. Solids **3**, 324 (1957).

[5] C. J. Gorter, G. J. Van Den Berg, and J. DeNobel, Can. J. Phys. **34**, 1281 (1956).

[6] J. E. Zimmerman and F. E. Hoare, J. Chem. Solids **17**, 52 (1960).

[7] J. E. Zimmerman and F. E. Hoare, Bull. Am. Phys. Soc. **3**, 124 (1958).