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A NEUTRON INELASTIC SCATTERING STUDY OF PHONONS IN METASTABLE BETA-GALLIUM

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Abstract.- The phonon dispersion curves of C-centred monoclinic beta-gallium at the melting temperature have been measured along five symmetry directions. The behaviour of the lower longitudinally polarised branch in the Ξ_X (S_X) direction suggests a desire to double the size of the unit cell. Initial model fitting calculations indicate that the interactions in β-Ga are of reasonably long range.

1. Experimental Measurements and Results.- The phonon dispersion curves of the stable orthorhombic α form of Ga were measured some years ago by Reichardt et al [1] and by Waeber [2]. In the present paper we discuss measurements and preliminary calculations of phonons in the metastable monoclinic β modification of this metal. The experimental details of this work are fully described elsewhere [3]. The main interest in β-Ga stems from its close structural and thermodynamic similarity to amorphous Ga and liquid Ga.

Three-axis spectrometer measurements were made using the IN2 and IN8 instruments at the ILL, Grenoble. Crystals were grown and oriented in situ, using a specially constructed goniometer and cryostat. Precautions were also necessary to reduce shock and vibration, in order to avoid accidental transformation to the stable α phase. Measurements were made at the melting temperature, 256.8K, in the symmetry directions Ξ_X (S_X), Δ, Ξ_Z, S_Z and R. Unusual features of the measured curves include the similar slopes of the three longitudinal acoustic branches, and the near mirror symmetry about (0.5,0,0) of the lower longitudinally polarised branch in the Ξ_X(S_X) direction (fig. 1). This latter feature suggests a desire to double the size of the unit cell by suppression of the C-centred lattice points.

2. Calculations.- The primitive unit cell contains 2 atoms. Its symmetry implies the following relationships between elements of the dynamical matrix $\underset{\sim}{D}$: $D_{\alpha\beta}(\underset{\sim}{q}11)=D_{\beta\alpha}(\underset{\sim}{q}22)$, and $D_{\alpha\beta}(\underset{\sim}{q}12)=D_{\beta\alpha}(\underset{\sim}{q}12)$. The submatrices $\underset{\sim}{D}(\underset{\sim}{q}kk)$ are symmetric and therefore real, in the absence of many-body forces.

In order to simplify the model fitting calculations we treated

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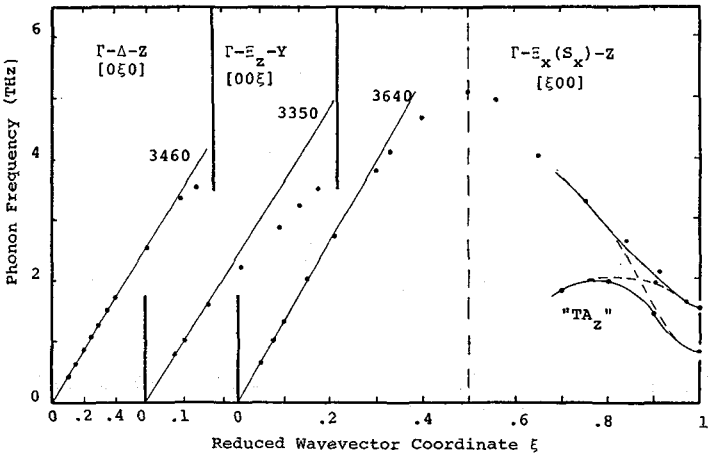

Fig. 1: The three longitudinal branches, with initial slopes in ms^{-1}. The likely behaviour of the low frequency [ξ00] branches for $\xi \geq 0.7$, were they to belong to different irreducible representations, is suggested by the broken lines.

the unit cell as orthorhombic: this is a reasonable approach since β is actually 92°, and no new degeneracies are introduced by making it 90°. On the other hand, the number of irreducible representations for a given q is in general increased. Within this approximation, β-Ga has the same structure as α-U [4], and the submatrices $\underset{\approx}{D}(qkk)$ are diagonal (in the absence of many-body forces) for the symmetry directions studied.

Initial attempts to fit the parameters of simple two-body potentials to the experimental results were not surprisingly unsuccessful. Furthermore, dispersion curves computed using real space pair potentials derived from a variety of pseudopotentials calculated for gallium [5,6,7] show little resemblance to experiment.

In the axially-symmetric force model there is a radial force constant $\phi_r(i)$ and a tangential force constant $\phi_t(i)$ for each shell of neighbours i. Experimental data for the five symmetry directions studied, no matter how precise or detailed they may be, are insufficiently "orthogonal" to determine all the force constants. For $i \leq 13$, eight of the force constants linking atoms on the same sublattice may be modified as follows: $\phi_{r,t}(1) \rightarrow \phi_{r,t}(1)+C, \phi_{r,t}(3) \rightarrow \phi_{r,t}(3)-C/2$, $\phi_{r,t}(10) \rightarrow \phi_{r,t}(10)-C$, $\phi_{r,t}(11) \rightarrow \phi_{r,t}(11)+C/2$, and six of the force constants linking atoms on different sublattices may be modified as follows: $\phi_{r,t}(2) \rightarrow \phi_{r,t}(2)+C', \phi_{r,t}(4) \rightarrow \phi_{r,t}(4)+C', \phi_{r,t}(7) \rightarrow \phi_{r,t}(7)-C'/2$ (where C and C' are independent and arbitrary), without in any way modifying $\underset{\approx}{D}$. It is therefore necessary to impose two arbitrary constraints, e.g. $\phi_r(11) = 0$, $\phi_r(7) = 0$.

Axially-symmetric force constant fits were made allowing interactions out to the 13th shell of neighbours, over a range of nearly

$6\mathring{A}$. With 92 independent data points the "best fit" was relatively poor, having a "goodness of fit" χ^2 of $\sim$ 12. This is not unexpected in view of the low symmetry of the system: the 13th shell in "orthorhombic" β-Ga (equivalent to the 19th shell in true monoclinic β-Ga) is only 2.15 times more distant than the nearest neighbour shell. Also the straightness of the longitudinal acoustic Δ and Ξ_x branches (fig. 1) implies the existence of reasonably long range forces.

3. Discussion.- The low symmetry and long range of interaction in β-Ga suggest that a reciprocal space analysis of the forces could be fruitful. Alternatively a "modified shell model" analysis, along the lines of Crummett et al's [4] calculations for α-U, may be worth pursuing. If at all possible we would like to find a unified description of the forces in α-Ga and β-Ga, in order to shed further light on the nature of the interactions between atoms in the liquid and amorphous states of this unusual but elusive metal.

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