

$$z = (1 + \eta + \eta^2 - \eta^3)/(1 - \eta)^3 \quad (4)$$

Assuming that for all simple fluids at the melting point $\eta_m = 0.45$, the values for z_m are calculated from (3) and (4) (see Table I).

Values of the self-diffusion coefficient for several liquid metals at their melting points were calculated with (2) using values of z_m from Table I. These values are compared with experimentally measured self-diffusion coefficients, along with the original self-diffusion coefficients calculated by Ascarello and Paskin using the correction factor $0.73(\eta_m/\eta)^{1/2}$ (see Table II).

The agreement of all calculated values with the melting-point data is remarkable, particularly when, as pointed out by Ascarello and Paskin, the error of the data is generally on the order of 10%.

The temperature dependence of (2) using (3) and (4) for gallium⁴ and tin⁵ is illustrated in Fig. 1.

It is observed that the Carnahan-Starling equation of state coupled with the backscattering correction of $0.73(\eta_m/\eta)$ yields a higher temperature dependence. Consequently, the data are more accurately represented over the full temperature range. Similar results have been obtained on comparing with available data for sodium,⁶ mercury,⁷ cadmium,⁸ lead,⁸ silver,⁹ and zinc.¹⁰ Data for indium⁵ compare better using (3).

In conclusion, the equation of state recently proposed by Carnahan and Starling yields the higher temperature dependence hoped for by Ascarello and Paskin. Experimental data over the entire temperature range appear to be much better represented for most liquid metals tested.

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¹H. Longuet-Higgins and J. Pople, *J. Chem. Phys.* **25**, 884 (1956).

²P. Ascarello and A. Paskin, *Phys. Rev.* **145**, 222 (1967).

³N. Carnahan and K. Starling, *J. Chem. Phys.* **51**, 635 (1969).

⁴E. Broome and H. Walls, *Trans. AIME* **245**, 739 (1969).

⁵G. Careri, A. Paoletti, and I. Vicentini, *Nuovo*

Cimento **10**, 1088 (1958).

⁶R. Meyer and N. Nachtrieb, *J. Chem. Phys.* **23**, 1851 (1955).

⁷E. Broome and H. Walls, *Trans. AIME* **242**, 2177 (1968).

⁸M. Mirshamsi, Ph.D. thesis, Oklahoma University, 1963 (unpublished).

⁹L. Yang, S. Kado, and G. Derge, *Trans. AIME* **212**, 628 (1958).

¹⁰W. Lange, W. Pippel, and F. Bendel, *Z. Physik Chem.* **212**, 238 (1959).

Temperature Dependence of the AuGa₂ Elastic Moduli

L. R. Testardi

Bell Telephone Laboratories, Murray Hill, New Jersey 07974

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An anomalously large temperature dependence of the elastic behavior of AuGa₂ occurs near 85°K. A singular exception (*c*₄₄-type shear) should provide some knowledge of the band responsible for the unusual elastic and magnetic behavior.

Numerous reports have now been published which indicate that the intermetallic compound AuGa₂ exhibits anomalies in its physical properties which are not shared by the isostructural compounds AuAl₂ and AuIn₂. The Ga⁷¹ Knight shift and spin-lattice relaxation times, and the magnetic susceptibility for AuGa₂ show a strong temperature dependence between 20 and 300°K.¹ The Seebeck coefficient of AuGa₂ has an unusual temperature

dependence in which the sign of the coefficient reverses at 14°K and again at 145°K.² These anomalies are not found in AuAl₂ and AuIn₂. However, the electrical resistivity,² the Hall coefficient,² the electronic and lattice specific heats,³ and the de Haas-van Alphen studies of the Fermi surface⁴ of these three compounds do not indicate any distinction of the AuGa₂ behavior.⁵ To explain the anomalies in the magnetic measurements, Jac-

TABLE I. Strains, elastic moduli, and peak temperature dependence of elastic moduli for AuGa₂.

Strain type	Propagation direction	Particle motion	Associated elastic moduli	(1/c) dc/dT _{extremum} (10 ⁻⁴ °K ⁻¹)
Longitudinal	[111]	[111]	$\frac{1}{3}(c_{11} + 2c_{12} + 4c_{44})$	-16 (min)
		[110]	$\frac{1}{2}(c_{11} + c_{12} + 2c_{22})$	-22 (min)
		[001]	c_{11}	-24 (min)
Shear	[111]	⊥[111]	$\frac{1}{3}(c_{11} - c_{12} + c_{44})$	-9 (min)
		[110]	$\frac{1}{2}(c_{11} - c_{12})$	-17 (min)
		[110]	c_{44}	-0.3 (max)
		[001]	c_{44}	-0.3 (max)
Volume	Bulk modulus	Elastic anisotropy	$\frac{1}{3}(c_{11} + 2c_{12})$	-23 (min)
			$(c_{11} - c_{12})/2c_{44}$	-17 (min)

carino *et al.*¹ have proposed a scheme in which the atomic character of the wave function of the itinerant electrons at the Fermi surface changes from *p*-like to *s*-like with increasing temperature. From augmented-plane-wave (APW) band-structure calculations, Switendick and Narath⁶ suggest that this change results from thermal effects on a high density-of-states band, located just below the Fermi level.

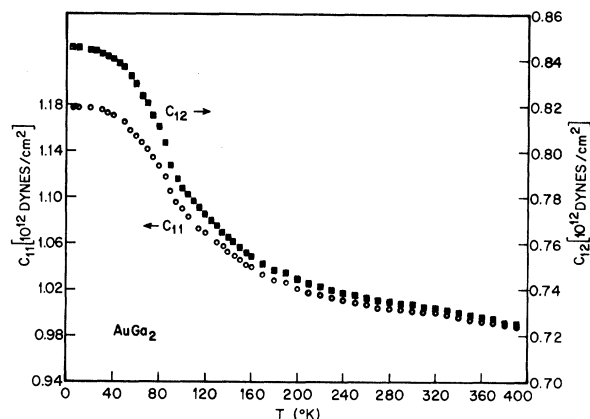
The elastic moduli give the general strain dependence of the internal (or free) energy. For effects which make a discernible contribution to the elastic moduli, the tensor nature of this property provides a means of establishing the anisotropy of the mechanism. For anomalies resulting from unusual features of the band structure, this anisotropy may be at least qualitatively predictable. The results discussed in this paper show that, in general, an anomalously large temperature dependence of the elastic behavior occurs around 85 °K. A singular exception (*c*₄₄-type shear) should provide some knowledge of the symmetry of the band responsible for the anomalous magnetic behavior.

The single crystal of zone-refined AuGa₂ was grown by Dorsi. The resistance ratio $R(300\text{ °K})/R(4.2\text{ °K}) = 225$. Cut and polished faces were prepared for sound propagation in $\langle 111 \rangle$ and $\langle 110 \rangle$ directions. The sound velocities *V* and elastic moduli *c* are related by

$$c = \rho V^2, \quad (1)$$

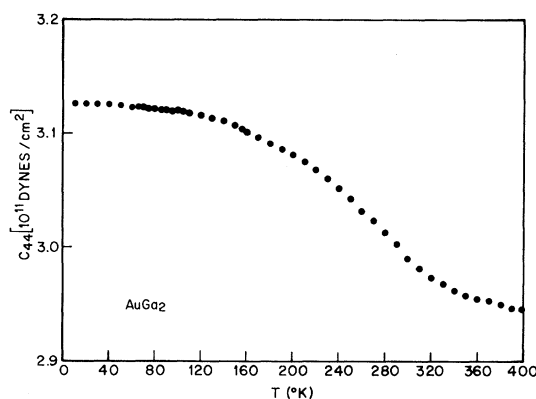
where the density $\rho = 9.92\text{ g/cm}^3$ has been calculated using the room-temperature x ray lattice parameter 6.074 Å .^{7,8} The elastic modulus tensor for a cubic crystal has three independent components, normally taken as *c*₁₁, *c*₁₂, and *c*₄₄. In Table I, we list the high symmetry waves and the associated elastic moduli. All five waves associated with $\langle 111 \rangle$ and $\langle 110 \rangle$ were used. From these velocities were obtained the three elastic moduli, with two redundant measurements used to check consistency.

Measurements of the sound velocity were made

FIG. 1. Temperature dependence of the elastic moduli *c*₁₁ and *c*₁₂ for AuGa₂ between 4.2 and 400 °K.

with an automated modification of the McSkimin pulse superposition method.⁹ The relative accuracy of the measurements, limited by nonideal sample-transducer bonds, was 3×10^{-4} to 10^{-5} over temperature intervals $\sim 50\text{ °K}$. The absolute accuracy, judged by the internal consistency of the data, was $\sim 0.3\%$.⁸

The elastic moduli *c*₁₁, *c*₁₂, and *c*₄₄ are shown as a function of temperature in Figs. 1 and 2. Two of these moduli exhibit an anomalous temperature dependence which can be seen from a plot of the logarithmic temperature derivative $(1/c)dc/dT$ shown in Fig. 3. This derivative shows a large negative peak at $T \approx 85\text{ °K}$ for *c*₁₁ and *c*₁₂, while for *c*₄₄ a much smaller peak of opposite sign occurs. For most solids, this derivative, starting from zero at $T = 0\text{ °K}$, decreases smoothly to about $-(1\text{ to }4) \times 10^{-4}$ at $T \sim 50$ to 100 °K , beyond which temperature it is relatively constant. Thus, for two of the elastic moduli an anomalously large

FIG. 2. Temperature dependence of the elastic modulus *c*₄₄ for AuGa₂ between 4.2 and 400 °K.

negative temperature coefficient occurs, which reaches an extremum at $T = 85^\circ\text{K}$.

Consider next the anisotropy of the anomalous temperature dependence. In Table I are listed the extremum values of $(1/c) dc/dT$ (which all occur at $T \approx 85^\circ\text{K}$) for the moduli associated with all longitudinal and shear strains along principal directions as well as the bulk modulus (for volume strains) and the elastic anisotropy. It is seen that, with one exception only, all $(1/c) dc/dT$ exhibit large extrema. The single exception is for $\{001\}$ planes sheared in a perpendicular direction¹⁰ (ϵ_4 strains) which, as noted, shows a small effect of opposite sign.

The adiabatic elastic moduli associated with strain ϵ are given by

$$c = \left(\frac{d^2 U}{d\epsilon^2} \right)_s, \quad (2)$$

where U is the internal energy and S is the entropy. We consider the suggestion of Switendick and Narath, that the temperature dependence of the magnetic properties is due to the presence of a band just below (by E_{gap}) the Fermi level. Letting X represent either the energy gap or the density of states of this valence band, we obtain for the modulus

$$c = c_0 + \left(\frac{d^2 U}{dX^2} \right)_s \left(\frac{dX}{d\epsilon} \right)_s^2 + \left(\frac{dU}{dX} \right)_s \left(\frac{d^2 X}{d\epsilon^2} \right)_s, \quad (3)$$

where c_0 is the "background" modulus having a typical temperature dependence $(1/c_0) dc_0/dT \sim -(1 \text{ to } 4) \times 10^{-4} (\text{K})^{-1}$ for $50^\circ\text{K} < T < 300^\circ\text{K}$. For high symmetry shear strains, we expect $dX/d\epsilon = 0$. The results of Table I show that, except for c_{44} , the elastic moduli for volume, longitudinal, and shear deformations in high symmetry directions show anomalies of comparable magnitude. Thus, the gap or density of states of the valence band responsible for the anomalous temperature dependence has a large strain dependence for all but $\langle 001 \rangle$ shear strains. Furthermore, since the anomalies for the longitudinal strains are compar-

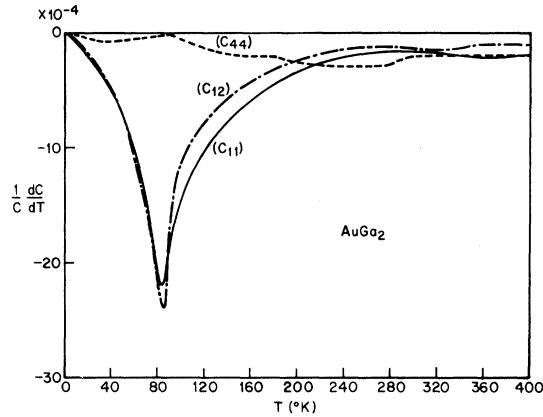


FIG. 3. Temperature derivatives (smoothed data) of the elastic moduli c_{11} , c_{12} , and c_{44} for AuGa₂ between 4.2 and 400 °K. For a normal solid this derivative increases from zero at $T = 0^\circ\text{K}$ to $-(1 \text{ to } 4) \times 10^{-4} (\text{K})^{-1}$ at $T \sim 50$ to 100°K , beyond which it is nearly constant.

able with those for the shear strains, it appears that the major contribution to the temperature dependence comes from the last term in Eq. (3).

One may also calculate the occurrence of extrema in $(1/c) dc/dt$ when $E_{\text{gap}}/kT \sim 1$ (very roughly) for valence bands whose density of states exhibit certain features near the band edge. For example, with a density of states proportional to E^n one finds, using exact statistics, an extremum in $(d/dT) \partial U / \partial E_g$ (and therefore dc/dt) at some temperature (of the order E_g/k) for $n < 0$. Similar results also occur for the number of carriers, magnetic susceptibility, etc. Quantitative results, however, depend upon the details of the valence-band structure.

From the elastic moduli at 4.2 °K, the calculated Debye temperature at 0 °K is found to be $(200.5 \pm 1)^\circ\text{K}$ using the tables of de Launey.¹¹ This compares favorably with the values $\Theta = (192 \pm 5)^\circ\text{K}^3$ and $\Theta = 196^\circ\text{K}^7$ from specific-heat measurements.

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¹V. Jaccarino, M. Weger, J. H. Wernick, and A. Menth, Phys. Rev. Letters **21**, 1811 (1968).

²J. P. Jan and W. B. Pearson, Phil. Mag. **8**, 279 (1963).

³J. A. Rayne, Phys. Letters **7**, 114 (1963).

⁴J. P. Jan, W. B. Pearson, Y. Saito, M. Springford, and I. Templeton, Phil. Mag. **12**, 1271 (1965).

⁵Only the resistivity and Hall coefficient extend over the temperature range where the anomalous magnetic behavior occurs.

⁶A. C. Switendick and A. Narath, Phys. Rev. Letters

22, 1423 (1969).

⁷J. H. Wernick, A. Menth, T. H. Geballe, G. Hull, and J. P. Marta, J. Phys. Chem. Solids **30**, 1949 (1969).

⁸No thermal expansion corrections were made. Normally these are an order of magnitude smaller than the velocity changes.

⁹H. J. McSkimin, J. Acoust. Soc. Am. **33**, 12 (1961).

¹⁰By symmetry this strain has the same modulus as that for $\{110\}$ planes sheared in a $\langle 110 \rangle$ direction.

¹¹J. de Launay, Solid State Phys. **2**, 285 (1956).