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Quasi-Harmonic Analysis of the Thermodynamic Data for Gold and an Estimate of $\Theta^M(T)$

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The moments of the Au frequency spectrum have been calculated in the usual manner from available thermodynamic data. These results are expressed in terms of the effective Debye temperatures, $\Theta^D(n)$. Unlike many materials, the values of $\Theta^D(n)$ for Au increase monotonically with increasing n. Values of the characteristic temperature associated with the Debye–Waller factor are determined [$\Theta^M(0, V_0) = 171 \pm 2\,^\circ\mathrm{K}$ and $\Theta^M(300, V_{300}) = 163 \pm 1\,^\circ\mathrm{K}$], and the temperature dependence of $\Theta^M(T, V_T)$ is estimated. Our results are compared with recent Mössbauer and X-ray data. The comparison with the Mössbauer measurements, which were performed at $4{\cdot}2 \leq T \leq 100\,^\circ\mathrm{K}$., yields a value of $\sim 4{\cdot}4$ for the internal conversion coefficient, α, for the 77 keV, γ-ray line of Au^{197}; this agrees well with a recent independent determination of $\alpha = 4{\cdot}23 \pm 0{\cdot}09$. However, our results for $\Theta^M(T, V_T)$ disagree, to within quoted estimates of error, with the results of published X-ray measurements. It is suggested that additional X-ray experiments extending to low temperatures would help to resolve these discrepancies.

Introduction

It is well known that the moments of the frequency spectrum can be determined, within the quasi-harmonic approximation, from an analysis of thermodynamic data; also, the Debye–Waller factor or its effective Debye temperature, $\Theta^M(T, V_T)$ can be estimated with reasonable accuracy from these moments. Our results for $\Theta^M(T, V_T)$ may be compared to very recent Mössbauer measurements and to previously published X-ray determinations of the Debye–Waller factor. We mention that Au was of special interest because relevant experiments for Au indicate that at room temperature, Θ^M is greater than the Debye temperature determined from elastic constants, Θ^E; this is contrary to what is found in other studied materials, as noted by Synecek, Chessin & Simerska (1970).

Calculations

The moments of the frequency spectrum are defined as follows:

$$\overline{\omega^n} = \int_0^\infty \{\omega^n G(\omega)\, d\omega\} \Big/ \int_0^\infty G(\omega)\, d\omega, \qquad (1)$$

where $G(\omega)$ is the lattice frequency distribution function. These moments can be related to an effective Debye temperature, $\Theta^D(n)$:

$$\Theta^D(n) = \frac{\hbar}{k} \left\{ \frac{1}{3}(n+3)\overline{\omega^n} \right\}^{1/n}, \quad \begin{matrix} n > -3\,, \\ n \neq 0 \end{matrix} \qquad (2)$$

where $\hbar$ and k have their usual meaning and the limits $n = -3$ and 0 exist. Low-temperature specific heat or elastic-constant data yield a value for $\Theta^D(-3)$ and Barron, Berg & Morrison (1957) have shown how the even, positive moments can be obtained from a high-temperature expansion of the specific heat Debye temperature, $\Theta^C(T)$; values of $\Theta^D(n)$ for $-3<n<0$ can be expressed in terms of integrals of the specific heat over temperature. The calculational procedures employed are essentially the same as those outlined by Barron *et al.* (1957) and Barron, Leadbetter, Morrison & Slater (1966).

The isobaric specific heat data (C_p) used in this analysis were taken from the compendium of Furukawa, Saba, & Reilly (1968); the values used represent principally the measurements of Martin (1964, 1966), Geballe & Giauque (1952), and Franzosini & Clusius (1963). The error in these C_p data is estimated at $<1\%$ below 5°K, $<0{\cdot}5\%$ for $5<T<30$°K, and $<0{\cdot}3\%$ for $30<T<300$°K. The C_p data were converted to isochoric specific heat (C_v) by the standard thermodynamic relation:

$$C_v = C_p\left(1 - \frac{\beta^2 T V_T}{C_p \chi_s},\right) \tag{3}$$

where β is the volume coefficient of expansion, V_T is the specific volume at temperature T, and χ_s is the adiabatic compressibility. Thermal-expansion data used were based on the measurements of Kos, Lamarche & Savary (1968) for $5<T<15$°K and of Nix & MacNair (1941), Fraser & Hollis Hallett (1965), and Leksina & Novikova (1963) for temperatures in excess of 15°K. The error in the coefficient of volume expansion is estimated at about 1% in the 5° to 15°K range (Kos *et al.*, 1968), about 5% for $15° < T < 110$°K and about 2% in the higher-temperature region. Values of the adiabatic bulk moduli were based on the temperature-dependent elastic-constant measurements of Neighbours & Alers (1958); the error in these moduli is estimated at less than 1·5%. The accuarcy of the values of β, V_T, and χ_s is not very critical since even at room temperature the C_v–C_p correction is less than 5% of C_p.

An electronic coefficient of $0{\cdot}729 \pm 0{\cdot}010$ mJ.°K^{-2}.mol^{-1}, determined by Furukawa *et al.* (1968), was used to correct for the electronic contribution to C_v. These corrected values of C_v were then used to evaluate the associated Debye temperature, $\Theta^C(T,V_T)$. The $\Theta^C(T,V_T)$ results were corrected for volume expansion using the approximation:

$$\Theta^C(T,V_0) = \Theta^C(T,V_T)\ (V_T/V_0)^{\gamma_D(2)},^{*} \tag{4}$$

where

$$\gamma_D(2) \equiv -\frac{\partial\{\ln \Theta^D(2)\}}{\partial\{\ln V\}}. \tag{5}$$

In the high-temperature region ($T > \Theta^C/2\pi$) for a quasi-harmonic crystal, $\Theta^C(T,V_0)^2$ can be expanded in a power series in T^{-2}. The temperature dependence of $\Theta^C(T,V_0)^2$ for Au can be adequately represented in this temperature range ($T < 120$°K$\approx \Theta/1{\cdot}5$) by the first two terms in this series. For $T > 120$°K the $\Theta^C(T,V_0)$ curve does not appear to be describable in terms of the quasi-harmonic approximation. This is not surprising since at these temperatures, Θ^C is quite sensitive to explicit anharmonic effects in C_v. At low temperatures an apparent anomolous behaviour of Θ^C has been noted previously (Martin, 1964). To obtain a rough estimate of the effects of this anomalous behaviour on our results, calculations were repeated with the removal of the small peak in Θ^C occurring at $T \sim 8$°K, keeping Θ_0^C fixed. Only negligible effects on our $\Theta^D(n)$ values were found. The primary results of our analysis are shown in the Barron plot for Au (Fig. 1).

It is known that the electron–phonon interaction may cause the electronic specific heat to be nonlinear in temperature over the temperature range in which we are interested [Hedin & Lundquist (1969) and references contained therein]. Unfortunately, to our knowledge, this effect in the electronic specific heat has not been treated for Au. However, it seems worth while to point out that in the temperature range of importance for our determination of the positive moments of the frequency spectrum, our estimate of the electronic spe-

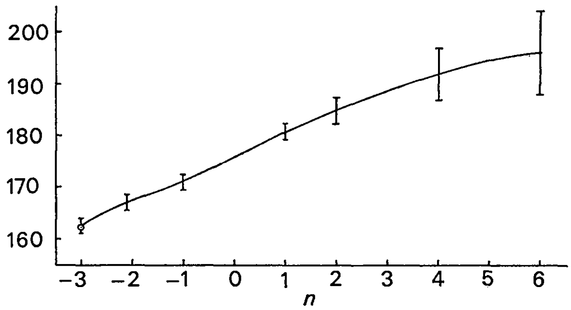

Fig. 1. Barron plot for gold, $\theta^D(n)$ *vs.* n at V_0. ⊙ $\theta^E(0, V_0)$ calculated from elastic constant data of Neighbours & Alers (1958). Bars correspond to our calculated values with the associated errors (see text). Curve is hand drawn through the calculated points.

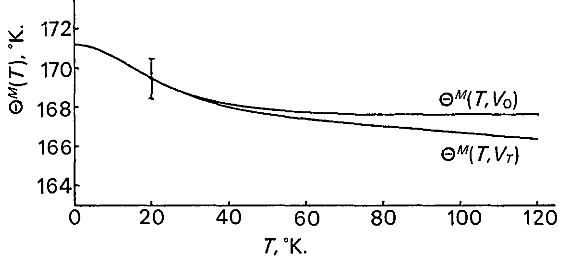

Fig. 2. Plot of θ^M *vs.* T Upper curve: $\theta^M(T, V_0)$; lower curve: $\theta^M(T, V_T)$. The error bar represents the error in our calculation over the entire temperature range.

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[*] Values of $\gamma_D(n)$ $(-3<n\leq 2)$ have been determined for the noble metals from an analysis of thermal expansion data; results are reported in a separate paper (Feldman & Skelton, 1971). For Au it was found that $\gamma_D(n)$ could be represented by a constant value of $2{\cdot}86 \pm 0{\cdot}30$.

cific heat corresponds to only a few tenths of a percent of the total specific heat for Au. Therefore, it seems unlikely that the values of these moments would be affected by explicitly taking account of the electron–phonon interaction. Further, in regard to the negative moments where low-temperature specific-heat data are important, it is encouraging that the values of Θ_0^C and Θ_0^E are in good agreement (Martin, 1964). For at very low temperatures, aside from the enhancement of the linear term, the electron–phonon interaction is expected to approximately lead to an extra T^3 term in the specific heat and hence to the inequality $\Theta_0^C \neq \Theta_0^E$.

The temperature dependence of $\Theta^M(T,V_0)$ was computed in the high- and low-tempearture regions using the appropriate expansions given by Salter (1965). The variation of $\Theta^M(T,V_T)$ at intermediate temperatures ($10<T<85$°K.) was found using the (3,3)-Padé approximant given by Salter (1965). A plot of $\Theta^M(T,V_0)$ is shown in Fig. 2 (upper curve); equation (4) with Θ^C replaced by Θ^M was used to determine the effects of volume expansion on Θ^M. [In general $\gamma_D(2)$ in equation (4) should also be replaced by $\gamma_D(-2)$.*] The resulting $\Theta^M(T,V_T)$ curve is also shown in Fig. 2 (lower curve). The comparison of our results at room temperature with corresponding experimental results is given in Table 1. Our estimated errors correspond to the quoted uncertainties in the specific-heat data and do not include possible uncertainties arising from our neglect of explicit anharmonic effects at low and moderate temperatures.

Table 1. *Comparison of values of Θ^M at $T=300$°K*

θ^M (°K.)	Method*	Authors
175 ± 5	I	Owen & Williams (1947)
177 ± 5	I	Alexopolous *et al.* (1965)
160 ± 6	II	
188 ± 4	I	Synecek *et al.* (1970)
188 ± 4	II	
168 ± 1	–	This work, V_0
163 ± 1	–	This work, V_{300}

* Method I: Computed from X-ray measurements from studies of the temperature dependence of $\theta^M(T, V_T)$. Method II: Computed from X-ray measurements by analyzing the variation of the scattered intensity with the Bragg angle.

Discussion

Erickson, Roberts & Thomson (1970) have recently measured the Mössbauer effect for the 77 keV γ-ray line of ^{197}Au in the temperature range $4{\cdot}2\leq T\leq 100$°K. A previous analysis of thermodynamic data has been used in conjunction with Mössbauer data to determine the internal conversion coefficient, α, of the 99 keV transition of ^{195}Pt (Feldman & Horton, 1965; Harris, Benczer-Koller & Rohnberg, 1965).† Neglecting the measurement of Erickson *et al.* at 100°K., we have found that excellent agreement between our $\Theta^M(T,V_T)$ curve and the Mössbauer data is obtained with $\alpha\simeq 4{\cdot}4$. (A more accurate value of $4{\cdot}37\pm0{\cdot}10$ was determined by Erickson *et al.* using our results.) Shirley, Kaplan & Axel (1961) have used theoretical values of the internal conversion coefficients in conjunction with measurements of the conversion electron intensities to estimate $\alpha=3{\cdot}96\pm0{\cdot}14$; employing a similar procedure, but with more recent theoretical and experimental data, Erickson *et al.* redetermined α at $4{\cdot}23\pm0{\cdot}09$. This recent value of α is in excellent agreement with our results.

Owen & Williams (1947), Alexopoulos, Boskovits, Mourikis & Roilos (1965), and Synecek *et al.* (1970) have evaluated $\Theta^M(T,V_T)$ at high temperatures ($T>290$°K.) from X-ray scattering measurements. As seen in Table 1, discrepancies exist among the various experimental values of $\Theta^M(300,V_{300})$. In method I (see Table), the temperature dependence of Θ^M is generally found to be consistent with thermal expansion effects alone. However, the values of $\Theta^M(300,V_{300})$ obtained by this method are apparently much larger than our calculated value in Table 1. On the other hand, the result of Alexopolous *et al.* (1965) using method II, with which our calculated value of $\Theta^M(300,V_{300})$ agrees, corresponds to a large positive value of $d\Theta^M/dT$ at high temperatures (see Table 1 of Alexopoulos *et al.*, 1965). We believe that additional X-ray experiments extending down to low temperatures might help in resolving the various discrepancies that we have noted.

It has been pointed out in the literature that $\Theta^M(300,V_{300})>\Theta^E(0,V_0)=\Theta^C(0,V_0)$ for Au, in contrast to what is found for other substances, Indeed, we have found that $\Theta^M(300,V_0)>\Theta^E(0,V_0)$ [although we have also found that $\Theta^M(300,V_{300})\sim\Theta^E(0,V_0)$]. In terms of our Barron plot this may be stated as $\Theta^D(-2)>\Theta^D(-3)$. Perhaps this inequality could have been predicted simply by inspecting the $\Theta^C(T)$ curve, since the lowest value of $\Theta^C(T)$ occurs at $T=0$°K. and since it seems reasonable to expect $\Theta^M(T,V_0)$ to lie within the range of $\Theta^C(T,V_0)$ values.

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* See Footnote marked * on p. 485.

† We wish to point. however. out that for $T\geq 30$°K. the specific heat data for Pt upon which this analysis was based was found to be in substantial disagreement with a subsequent measurement (Shoemaker & Rayne, 1968, *Phys. Rev.* **26**A, 222).

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X-ray Scattering and the Chemical Bond in N_2 and CN^-

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X-ray scattering from the chemical bond within N_2 and CN^- has been studied in detail. Differences in scattering from these systems, derived from bonding and non-bonding models, are characterized by R values of $\sim 0{\cdot}04$. Partitioning of the scattering into core and valence electron parts clearly demonstrates that the bonding effects are completely situated in the valence electron structure of the systems. Therefore, new evidence has been contributed to support valence structure analysis methods presently employed in X-ray diffraction structure studies.

Introduction

The molecular form-factor formalism, introduced in a previous paper (Groenewegen & Feil, 1969, henceforth referred to as G & F), resolves the electron density in solid-state structures in terms of molecules instead of atoms. This means that the scattering by a molecule is no longer given by the well known equation

$$f_{\text{molecule}}(\mathbf{s}) = \sum_{\substack{i \text{ atoms in} \\ \text{the molecule}}} f_i \exp\,(i\mathbf{s}.\mathbf{r}_i) \qquad (1)$$

in which $\mathbf{s}=\mathbf{k}-\mathbf{k}_0$ with $\mathbf{k}_0$ and $\mathbf{k}$ the wave vectors of the incident and scattered beam respectively, $f|_i$ is the atomic form factor and $\mathbf{r}_i$ is the position coordinate with respect to a common origin, of atom i. Instead, use is made of the basic equation

$$f(\mathbf{s}) = \langle\psi|\sum_{i=1}^{N} \exp\,(i\mathbf{s}.\mathbf{r}_i)\,|\psi\rangle \qquad (2)$$

where ψ is the state function of the N electron system of the molecule and $\mathbf{r}_i$ denotes the ith position coordinate. In this way bonding effects in the electron distribution are taken care of. Groenewegen & Feil developed and succesfully applied this method to NH_4F to study the chemical bond within the NH_4^+ ion. Recently, the topic of the chemical bond in X-ray (and electron) diffraction structure analysis has received considerable attention, and various methods have been proposed and tried to solve the problem (Coppens, 1968; Stewart, 1968, 1969; Bonham, 1969; Harkema & Feil, 1969). This paper presents some new results obtained along the lines developed by G & F. The chemical bond in N_2 and CN^- is shown to be observable by X-ray diffraction. A preliminary report on this part has been given elsewhere (Groenewegen, 1969; Zeevalkink, 1970).

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