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Measurements of the Thermal Variation of the X-ray Debye Temperature of Pure Nickel and Chromium* †

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The X-ray Debye temperature has been determined from integrated X-ray intensity data for single crystals of nickel and chromium in the temperature range 100°K < T < 520°K. The data were corrected for thermal diffuse scattering as well as changes in the lattice parameters. The room temperature values of the Debye temperature were found to be 410° ± 10°K and 545° ± 20°K for nickel and chromium, respectively. This is in agreement with already published values for nickel; chromium, however, appears to give a room temperature Debye temperature which is somewhat lower than has been previously reported.

In the case of both metals, the elastic constant Debye temperature was computed from the available elastic constant data. In both cases, the elastic constant Debye temperature, Θ_E, was found to be greater than the X-ray Debye temperature, Θ_M. This is in agreement with previously reported values for nickel; in contradiction to published results, however, chromium was found to conform to the general relation that $\Theta_E/\Theta_M > 1$.

Introduction

Debye temperatures are frequently used to characterize the thermal vibrations of a solid and are found to be useful parameters in a number of physical properties of solids. Herbstein (1961) has recently reviewed the methods of measuring Debye temperatures and has discussed the reasons for the different values obtained from different physical measurements.

One means for determining the Debye temperature is through studying the intensity of a Bragg reflection in X-ray diffraction. The integrated Bragg intensities have been measured over a wide temperature range. From these intensity measurements, the thermal variation of the Debye temperature has been obtained.

These methods have been applied to nickel and chromium; the room temperature results for nickel compare favorably with X-ray Debye temperatures reported by Simerska (1962) and Goldak (1965). Chromium, however, seems to give a somewhat lower X-ray Debye temperature than has been reported by Ilyina & Kristskaya (1955).

Theory

The basic theory employed in this work was developed by several authors. Our notation is similar to that of James (1954) where a detailed development and references can be found. The relation developed for the scattered X-ray intensity is given by the following expression:

$$\langle I(\bar{S}/\lambda)\rangle = C|f_o|^2\, e^{-2M} I_0(\bar{S}/\lambda) + I_2(\bar{S}/\lambda) \tag{1}$$

where

$$2M = \frac{12\,.\,h^2}{mk\Theta_M}\left\{\frac{F(X)}{X} + \frac{1}{4}\right\}\left(\frac{\sin\theta}{\lambda}\right)^2; \tag{2}$$

$$F(X) = \frac{1}{X}\int_{\xi=0}^{X} \xi\,(e^{\xi}-1)^{-1}d\xi;\; X = \frac{\Theta_M}{T}; \tag{3}$$

$$C = (e^2/mc^2)^2\,\frac{1+\cos^2 2\theta}{2R^2}; \tag{4}$$

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e and m are the electronic charge and mass, respectively; c is the velocity of light; θ is the scattering angle; R is the distance from the crystal to the point where the scattered wave is being observed; T is the temperature; Θ_M is the X-ray Debye temperature; f_0 is the atomic scattering factor; $\bar{S}$ is the diffraction vector; λ is the wavelength of the incident radiation; e^{-2M} is the Debye–Waller factor.

The $I_0(\bar{S}/\lambda)$ term in equation (1) describes the Bragg scattering intensity, *i.e.* the scattering that would result if the atoms were 'frozen' in their equilibrium positions. The second term, $I_2(\bar{S}/\lambda)$, which would vanish in this frozen situation, is interpreted as the one phonon thermal diffuse scattering intensity, hereafter referred to as T.D.S. We are primarily interested in the variation of the Bragg scattering with temperature, and therefore must calculate analytically the integrated intensity due to the T.D.S. and subtract this result from the total measured intensity. Nilsson (1957), starting from Waller's (1928) original treatment, has developed a method of correction for the T.D.S. from single crystals assuming no mosaicity. We have taken the expressions developed by Ramachandran & Wooster (1951) and devised a technique for simultaneously integrating the averaged T.D.S. intensity over the X-ray detection window and over the 2θ motion. This correction is to second order in the T.D.S., taking into consideration the mosaicity of the specific crystal being investigated. The calculation is believed to be of sufficiently general interest to warrant an independent treatment; a complete development of this correction in conjunction with a set of tables for a variety of experimental situations is in preparation for submission to *Acta Crystallographica*.

To correct for volume expansion effects in the Bragg diffraction angle and in the atomic scattering factor, we used our values for the changes in the lattice parameter for nickel and the data of Bolef & de Klerk (1963) for chromium.

We shall, in all cases, restrict ourselves to a specific set of crystal planes and a specific type of incident radiation; let us, therefore, change the functional notation from $I(\bar{S}/\lambda)$ to $I(T)$. Noting that the Debye–Waller factor is also temperature dependent, we shall write it as $e^{-2M(T)}$. Writing equation (1) for two different temperatures, T_0 and T, dividing the one by the other and taking the natural logarithm of the quotient yields the following:

$$2M(T) - 2M(T_0) = \ln\left[\frac{\langle I(T_0)\rangle \text{meas.}}{\langle I(T)\rangle \text{meas.}}\right]. \qquad (5)$$

We are now in a position to compute the Debye temperature, $\Theta_M(T)$, from the experimental data and a 'guessed' value of the reference Debye temperature, *i.e.* a hypothesized value of the Debye temperature, at T_0. From this we can determine, by means of equations (2) and (3), a value for $2M(T_0)$. Equation (5) is then used to evaluate $2M(T)$ and finally equations (2) and (3) allow determination of the actual Debye temperature, $\Theta_M(T)$. This entire numerical calculation along with the necessary corrections on the data was performed on an IBM 1620-II computer.

Experimental methods

The data on both nickel and chromium were taken on a General Electric XRD-5 diffraction unit. With the use of a molybdenum X-ray tube, the highest order peaks parallel to the (110) face were examined for large single crystals of nickel and chromium. The highest order peaks were selected because the effects of surface irregularities and extinction are minimized at large scattering angles. In addition, the ω-scan was used as a quality check for the surface condition of the portion of the crystal being irradiated. As pointed out by Furnas (1957), along with the general peak shapes, the ω-scan is perhaps the most sensitive to the surface conditions of the crystal; a half-width of more than 0·65° was deemed unsatisfactory.

All integrated intensity measurements were made in precisely the same manner. Under maximum peak conditions in ω and χ, the 2θ-peak was scanned at a scanning rate of 0·2° min^{-1}, while the intensity was simultaneously counted by a General Electric 5-SPG proportional counter tube and recorded on a General Electric SPG Speedomax Recorder Chart. In all cases, the first measurement made in any given day was done at room temperature; this was then used as the reference value for all subsequent data taken that day. At the end of a series of thermal variations, the room temperature situation was restored and checked for any possible changes.

The thermal temperatures were measured by two iron–constantan thermocouples cemented to the upper and lower portions of each of the two crystals – thus affording a means of detecting any possible thermal gradients. The maximum error in the temperature measurement is estimated to be ±5°K.

To rule out the possibility of extinction effects altering the thermal variations of the integrated intensity ratios and hence of the Debye temperatures, the thermal variation of these intensities was examined for more than one diffraction peak. No significant difference was noted in the thermal variation of the data.

Computations

In order to calculate the Debye temperature from the experimental data, we must, as already mentioned, assume a value for the reference Debye temperature, $\Theta_M(T_0)$, hereafter referred to as R.D.T.; the reference temperature, T_0, is taken to be 298°K. As pointed out by Chipman (1960), $\Theta_M(T)$ at low temperatures is highly sensitive to the choice of the R.D.T. One chosen too high will cause large negative slopes in the low temperature region in the plot of Θ_M *versus* T, while a low R.D.T. will result in positive slopes in the same region. However, no substantial change in the high temperature slopes is noted. These conditions were found to be true in the case of both nickel and chromium. Curves of Θ_M *versus* T corresponding to three choices of the R.D.T. along with the actual data are plotted in Fig. 1 for nickel and in Fig. 2 for chromium.

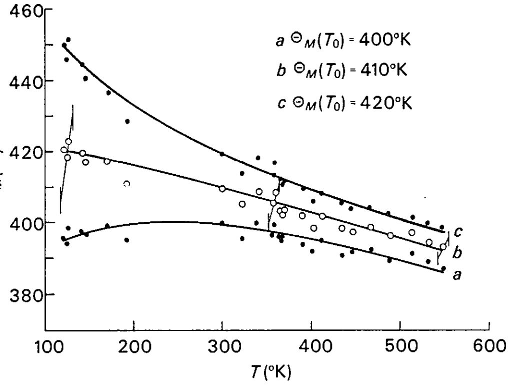

Fig. 1. Debye temperature *versus* temperature for nickel.

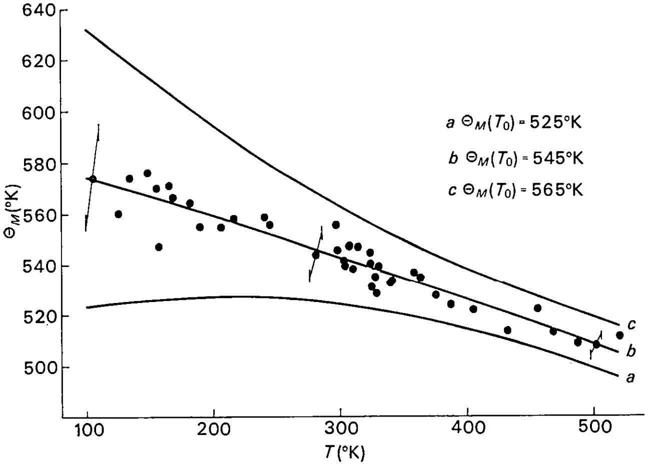

Fig. 2. Debye temperature *versus* temperature for chromium.

From theoretical calculations of X-ray Debye temperatures (Salter, 1965), it seems unreasonable to expect an abrupt change in the slope of the Θ_M *versus* T plot in the temperature regions under consideration. On this basis, we contend that the only reasonable values for the R.D.T. must lie in the range from 400° K to 420° K for nickel and from 525° K to 565° K for chromium.

Most of the accountable errors have already been compensated for, as discussed previously. The two largest uncompensated errors are believed to be the uncertainty in the measurement of the temperature, which, as already mentioned, is taken to be ± 5° K, and the uncertainty in the determination of the integrated intensity; this error is estimated to be $\pm 1\%$ of the measured intensity. These errors are probably the predominant ones involved and their estimated magnitudes were used to determine the experimental limits of the Debye temperatures based on a chosen R.D.T. We have selected a R.D.T. for nickel of $410° \pm 10°$ K and a R.D.T. for chromium of $545° \pm 20°$ K; the error bars shown on the graphs then represent the experimental limits of error based on these R.D.T.'s.

Furthermore, we find that for all reasonable values of the R.D.T., the high temperature Debye temperatures can be fit to an equation of the following form:

$$\frac{\Delta\Theta}{\Theta(T_0)} = \alpha T + \beta$$

where $\Delta\Theta = \Theta_M(T) - \Theta_M(T_0)$; $\alpha_{\mathrm{Ni}} = -1{\cdot}75 \times 10^{-4}$ (°K)$^{-1}$, $\beta_{\mathrm{Ni}} = 0{\cdot}0537$ and $\alpha_{\mathrm{Cr}} = -3{\cdot}28 \times 10^{-4}$ (°K)$^{-1}$, $\beta_{\mathrm{Cr}} = 0{\cdot}0966$.

Discussion

For nickel, the reference value of the Debye temperature, *i.e.* the room temperature value, was determined to be $410° \pm 10°$ K. As seen in Table 1, this result com-

Table 1. *Comparison of the room temperature Debye temperature, Θ_M^*, of nickel and chromium as determined by various methods*

Material	Θ_M	Method	Source
Nickel			
	478°K	Elastic constants (C_{ij}) from ultrasonic measurements	Our calculations based on data of Alers, Neighbours & Sato (1960)
	445	Elastic constants from Young's modulus	Herbstein (1961)
	350	X-ray diffraction from crystalline powder	Ilyina & Kristskaya (1955)
	405	X-ray diffraction from crystalline powder	Simerska (1962)
	431	X-ray diffraction from crystalline powder	Zhuravlev & Katsnel'son (1959)
	423	X-ray diffraction from crystalline powder	Goldak (1965)
	410	X-ray diffraction from single crystal	This work
Chromium			
	602	Elastic constants (C_{ij}) from ultrasonic measurements	Our calculations based on data of Bolef & de Klerk (1963)
	466	Elastic constants from Young's modulus	Herbstein (1961)
	512	Specific heat	Clusius & Franzosini (1962)
	580	X-ray diffraction from crystalline powder	Ilyina & Kristskaya (1955)
	545	X-ray diffraction from single crystal	This work

* Θ_M refers to averaging the Debye temperature over the reciprocal square of the transverse and longitudinal modes, appropriate to diffraction measurements, whereas Θ_D refers to averaging over the reciprocal cube, appropriate to specific heat and elastic constant measurements. As pointed out by Zener & Bilinsky (1936), these two average Debye temperatures can be related through Poisson's ratio. This relationship has been used to convert all Θ_D values to equivalent Θ_M values for purposes of comparison.

pares quite favorably with recently published values determined by the same method.

The Debye temperature at room temperature for chromium was found to be 545° ± 20° K. As Table 1 shows, this value is about 35° lower than that reported by Ilyina & Kristskaya (1955); however, these authors have stated that, in consideration of melting point data and self diffusion coefficients, their value of the Debye temperature seems inordinately high.

As reported by Bacon (1961), neutron diffraction data have indicated that chromium undergoes a transition from a paramagnetic to an antiferromagnetic state at 310° K. An anomaly also shows up around room temperature in the specific heat data, as Beaumont, Chihara & Morrison (1960) have reported a lambda type anomaly at 38·5° ± 0·3° C. Further, Bolef & de Klerk (1963) have found that this anomaly shows up in the thermal variation of the elastic constants as well. As seen in Fig. 2, if the anomaly does show up in the X-ray Debye temperature, it is within our limit of error. Calculations from the elastic constant data indicate that one should expect about a 3° change in the Debye temperature at the Néel temperature.

Our data for nickel give a thermal variation of the Debye temperature in agreement with the limited data of Simerska (1962). There are no published data on the thermal variation of the Debye temperature as determined by X-ray diffraction techniques for chromium. However, the variation for chromium is similar in form and appears to follow the general form for most metals for temperatures increasing from 100° K.

For many solids, the elastic constant Debye temperature is found to be greater than the X-ray Debye temperature; this is evidenced by the results summarized by Gschneidner (1964). The only exception to this relation for all the elements found in Gschneidner's table is in the case of chromium, *i.e.* the value of the Debye temperature computed from Köster's (1954) polycrystalline elastic constants falls below the X-ray Debye temperature as determined by Ilyina & Kristskaya (1955). It is suggested by Herbstein (1961) that the X-ray results are in question.

We have calculated the Debye temperature from the elastic constant data on these metals, using an isotropic average velocity of the vibrational waves in conjunction with Reuss & Voight isotropic averages of the elastic constants (Huntington, 1958). Admittedly these isotropic conditions do not exist in the real crystal; however, such an approximation is not unreasonable (Anderson, 1963). Using the ultrasonic data of Alers, Neighbours & Sato (1960) for nickel and that of Bolef & de Klerk (1963) for chromium, as seen in Table 1, we find a room temperature elastic constant Debye temperature of 478° K for nickel and of 602° K for chromium. The results for nickel are consistent with the phenomenological relation $\Theta_E > \Theta_M$. However, for chromium, this value of the Debye temperature is much larger than the Debye temperature calculated from the polycrystalline data. Recognizing that the ultrasonic experiments of Bolef & de Klerk were very carefully performed over a broad range of temperatures, and in consideration of our results, it is our contention that the generalization that the elastic constant Debye temperature is greater than the X-ray Debye temperature is valid for chromium as well as for nickel.

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