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Debye temperatures of oxides with the NaCl structure

The characteristic Debye temperature is an important parameter which features in descriptions of the thermal and elastic properties of a solid. Traditionally, Debye temperatures (calorimetric, θ_{cal}) are obtained from heat capacity measurements, but values may also be calculated from elastic constants (θ_{el}). A number of high precision techniques for the latter procedure have been reviewed by Alers [1], and Konti and Varshni [2]. At temperatures close to absolute zero θ_{cal} is usually very close to θ_{el}.

Debye temperatures have been published for a wide variety of solids [1–4], but despite their relative simplicity, there are only limited data for oxides having the NaCl structure. Elastic constants of varying reliability are now available for most of these oxides and thus θ may be readily calculated.

By considering only acoustic branches of the phonon dispersion spectrum of a diatomic solid, the elastic Debye temperature at 0 K may be approximated to

$$\theta_{\text{el}} = \frac{h}{k}\left(\frac{3pN\rho}{4\pi M}\right)^{1/3} \cdot V_{\text{m}}, \qquad (1)$$

where h is Planck's constant, k is Boltzmann's constant, p is the number of atoms in the molecule (i.e. 2 in this case), N is Avogadro's number, ρ is density, M is molecular weight and V_{m} is the mean sound velocity defined by

$$V_{\text{m}} = \left(\frac{1}{3}\sum_{i=1}^{3}\int_{V}\frac{1}{V_i^3}\frac{\mathrm{d}\Omega}{4\pi}\right)^{-1/3}, \qquad (2)$$

i.e. the average of all the direction-dependent velocities V_i [3]. When the individual elastic moduli are available, the integral in Equation 2 may be solved by using one of the high precision techniques [1, 2].

Alternatively, for isotropic crystals, an approximate value may be obtained from

$$V_{\text{m}} = \left[\frac{1}{3}\left(\frac{2}{V_{\text{s}}^3}+\frac{1}{V_{\text{p}}^3}\right)\right]^{-1/3}, \qquad (3)$$

where V_{s} and V_{p} are the transverse sound velocity and longitudinal sound velocity, respectively [3].

TABLE I Elastic moduli, densities and calculated Debye temperatures of some NaCl structure oxides

Oxide	Elastic moduli ($\times 10^{10}$ Nm^{-2})			Density ($\times 10^3$ kg m^{-3})	Reference	$\theta_{\text{(calc)}}$ (K)
	C_{11}	C_{12}	C_{44}			
BaO	12.440	4.869	3.368	5.992	[5]	292.3
SrO	17.354	4.715	5.587	5.009	[5]	441.4
CoO	25.911	14.87	8.268	6.438	[6]	517.8
MnO	22.3	12.0	7.90	5.39	[7]	525.7
CaO	22.063	5.655	8.032	3.346	[5]	673.6
MgO	29.404	9.248	15.581	3.579	[8]	939.1

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TABLE II Sound-wave velocities, densities and calculated Debye temperatures of some NaCl structure oxides

Oxide	V_s (km sec^{-1})	V_p (km sec^{-1})	Density ($\times 10^3$ kg m^{-3})	Reference	$\theta_{(calc)}$ (K)
NiO	1.959	6.137	6.801	[9]	317.4
CdO	2.62^a	4.70^a	8.239^b	[10]	369.6

^{a}Values estimated from graph.
^{b}From [11].

Although Equation 1 is only strictly valid at 0 K, it is commonly used to estimate values of θ at higher temperatures [3].

Using published elastic moduli, Debye temperatures have been calculated by the single approximation Fedorov method explained in [4] for BaO, SrO, CoO, MnO, CaO and MgO. The results are listed in Table I. Of the remaining oxides, V_s and V_p are available for CdO and NiO, and calculated θ based on Equations 1 and 3 are shown in Table II. For consistency, all the experimental data listed in Tables I and II refer to measurements made at or near 298 K.

Konti and Varshni [2] noted that for families of alkali halides, linear trends existed between θ_{el} and the reduced mass (μ). The equivalent data for the NaCl structure oxides also yield a similar relationship, but it has no theoretical basis. However, the phonon dispersion spectrum of a simple diatomic crystal has optical branches which satisfy

$$\omega^2 = \frac{2C}{\mu} \tag{4}$$

at the Brillouin zone centre [12]. Here, C is a force constant and ω the angular frequency ($= 2\pi f$) corresponding to infra-red absorption. It should therefore be possible to define another θ in terms of the infra-red absorption frequency for each oxide and this should be proportional to $(\mu)^{-1/2}$ [13]. A relationship of this type is also obeyed for the present θ_{el} data, with the exception of the result for NiO (Fig. 1), but the high degree of linearity may be fortuitous. The calculated θ_{el} for NiO (Table II) is significantly lower than an early result of 404 K for θ_{cal} [14]. Notis, Spriggs and Hahn [9] reported that sound velocity measurements for this oxide yielded an exceptionally low V_m and an exceptionally high Poisson ratio. The properties of NiO may therefore be anomalous.

In view of the apparently simple relationship between θ_{el} and μ it should be possible to estimate Debye temperatures of oxides for which V_m are not available. For example, from Fig. 1, θ_{el} for FeO would be 535 K. Recent measurements on single crystal $Fe_{0.92}O$ [15] indicate that sound-wave velocities in stoichiometric FeO ($\rho = 5860$ kg m^{-3})

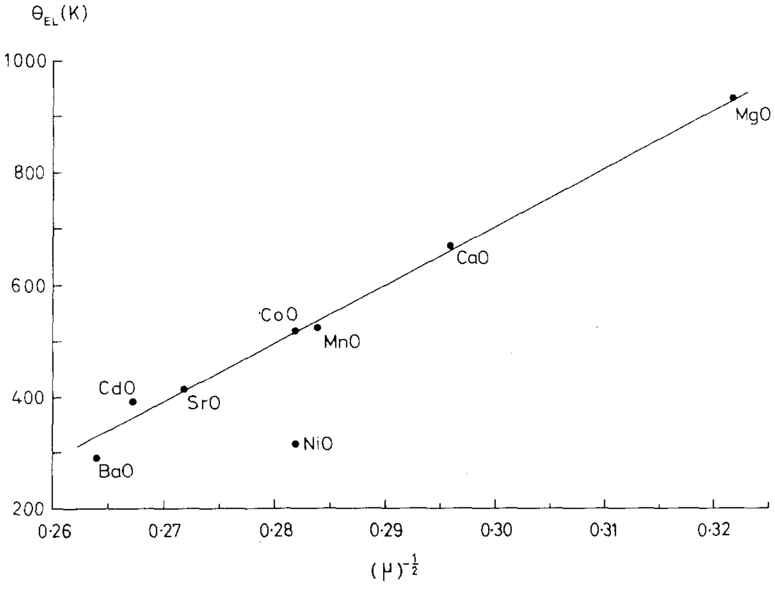

Figure 1 Plot of Debye temperature (θ_{el}) against (reduced mass, in amu)$^{-1/2}$ for NaCl structure oxides.

will be approximately 6.63 km sec^{-1} for V_p and 3.23 km sec^{-1} for V_s. These data give a Debye temperature of 494 K which is in satisfactory agreement with the above value.

With the exception of perhaps NiO, the elastic Debye temperatures of the NaCl structure oxides form an internally consistent set of data and follow a simple relationship involving the reduced mass.

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The effects of alkali-earth metal ions on the crystalline state of ZnO

The doping effects of alkali-earth metal ions (Mg^{2+}, Ca^{2+}, and Sr^{2+}) on the crystalline state of ZnO were studied using X-ray diffraction methods. The samples were sintered in air at 1200° C for 5 h. X-ray powder diffraction measurements were carried out with Ni-filtered Cu*Kα* radiation.

Fig. 1 shows the results for the lattice parameters and axial ratio. Fig. 1a shows these results for Mg-doped ZnO. The lattice parameter, a, for Mg-doped ZnO increased linearly up to about 5 mol% Mg, which agreed with the solubility limit reported by Segnit and Holland [1]. The lattice parameter, c, on the other hand, decreased until 15 mol% Mg, far exceeding the solubility limit of 5 mol% Mg. Accordingly the axial ratio, c/a, decreased with the increase of MgO. Fig. 1b shows the results for Ca-doped ZnO. Doping with Ca ions resulted in the increase of the both of a and c up to about 1.5 mol% Ca, but the increase of a was much more marked than that of c, and thus the value of c/a decreased sharply in this region. Doping ZnO with Sr ions, Fig. 1c, did not cause any significant changes in a or c. The change of c/a with Mg-content up to 5 mol% is considered to be due to the disolution of Mg ions in the ZnO lattice. It is worthy of notice that the axial ratio, c/a, continues to decrease even after the Mg-content exceeds the solubility limit of 5 mol%. Since c/a for ZnO is said to depend on the surface condition of the crystals [2], this effect is attributed to an interaction between the ZnO lattice and the segregated MgO on the grain boundaries. The solubility of Ca ions in the ZnO lattice is evaluated to be about 1.5 mol% from the lattice parameter data (Fig. 1b). The absence of any apparent change in the lattice parameters as a result of Sr addition indicates that the solubility of Sr ions in

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