therefore valid for all alkali cyanides with quasi rock salt structure.

(iv) The differences between cyanides and chlorides observed here again confirm the suggestion, derived from an earlier investigation on alums (Haussühl & Preu, 1978), that the replacement of highly symmetrical ions like chlorine anions by asymmetric ions causes systematic changes in TOEC in the sense that the ratios $c_{111}/c_{123}$ and $c_{111}/c_{112}$ are strongly reduced by lowering $c_{111}$ and increasing $c_{112}$ and $c_{123}$. This indicates that the 'transverse' interactions, which are connected with the value of Poisson's ratio, are strengthened.

A quantitative interpretation of the nonlinear elastic behaviour of the alkali cyanides of rock salt type is expected to be obtained from a further development of the dynamical models in which the coupling of rotational movements of the cyanide ions with translational modes of the lattice is introduced (Bill, Jex & Müllner, 1976; Michel & Naudts, 1977; Mokross & Pirc, 1978; Rehwald, Sandercock & Rossinelli, 1977). Our results with respect to the fluid-like behaviour might support efforts to establish a simple model for the librational–transverse interactions in fluids.

### References

BARTELS, R. A. & SCHUELE, D. E. (1965). *J. Phys. Chem. Solids*, **26**, 537–549.

BILL, C. J., JEX, H. & MÜLLNER, M. (1976). *Phys. Lett. A*, **56**, 320–322.

BRUGGER, K. (1965*a*). *J. Appl. Phys.* **36**, 759–768.

BRUGGER, K. (1965*b*). *J. Appl. Phys.* **36**, 768–773.

DRABBLE, J. R. & STRATHEN, R. E. B. (1967). *Proc. Phys. Soc. London*, **92**, 1090–1095.

DULTZ, W. & KRAUSE, H. (1978). Private communication.

DULTZ, W., KRAUSE, H. & WINCHESTER, L. W. JR (1977). *J. Chem. Phys.* **67**, 2560–2566.

ELKIN, S., ALTEROVITZ, S. & GERLICH, D. (1970). *J. Acoust. Soc. Am.* **47**, 937–939.

HAUSSÜHL, S. (1957). *Naturwissenschaften*, **44**, 325.

HAUSSÜHL, S. (1960). *Z. Phys.* **159**, 223–229.

HAUSSÜHL, S. (1967). *Phys. Kondens. Mater.* **6**, 181–192.

HAUSSÜHL, S. (1973). *Solid State Commun.* **13**, 147–151.

HAUSSÜHL, S., ECKSTEIN, J., RECKER, K. & WALLRAFEN, F. (1977). *Acta Cryst.* A**33**, 847–849.

HAUSSÜHL, S. & PREU, P. (1978). *Acta Cryst.* A**34**, 442–446.

HOCHHEIMER, H. D., LOVE, W. F. & WALKER, C. T. (1977). In *High Pressure Low Temperature Physics*. New York: Plenum.

MICHEL, K. H. & NAUDTS, J. (1977). *J. Chem. Phys.* **67**, 547–558.

MOKROSS, B. J. & PIRC, R. (1978). To be published.

REHWALD, W., SANDERCOCK, J. R. & ROSSINELLI, M. (1977). *Phys. Status Solidi A*, **42**, 699–705.

SWARTZ, K. D. (1967). *J. Acoust. Soc. Am.* **41**, 1083–1092.

THURSTON, R. N. & BRUGGER, K. (1964). *Phys. Rev.* **133**, A1604–A1612.

WALLACE, D. C. (1970). *Solid State Phys.* **25**, 301–404.

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# SHORT COMMUNICATIONS

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## Lindemann's rule and the X-ray Debye temperature of anisotropic Zn and Cd single crystals.

By ELISABETH ROSSMANITH, *Mineralogisch–Petrographisches Institut der Universität Hamburg,* 2000 *Hamburg* 13, *Grindelallee* 48, *Federal Republic of Germany*

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### Abstract

Lindemann's rule was applied to Zn and Cd single crystals and found to be valid for these solids, $x_Z$ being in the range 0·2 to 0·25.

### Introduction

As pointed out by Ziman (1965), the basic assumption of Lindemann's rule of melting is that melting occurs if the ratio of the amplitude of atomic vibration to the radius of the space occupied by the atom in the solid reaches a certain value. This fraction seems to be a constant for all monatomic solids.

The mean-square displacement in a particular direction of the atoms in solids is given by (James, 1948, p. 220)

$$\bar{u}^2 = \frac{3\hbar^2 T}{mk\Theta^2}\left[\varphi\left(\frac{\Theta}{T}\right) + \frac{\Theta/T}{4}\right] \qquad (1)$$

where $\hbar = h/2\pi$, $h$ = Planck's constant, $k$ = Boltzmann's constant, $\Theta$ is the Debye temperature, $m$ the absolute mass of the atom, $T$ the absolute temperature and the function

$$\left[\varphi\left(\frac{\Theta}{T}\right) + \frac{\Theta/T}{4}\right]$$

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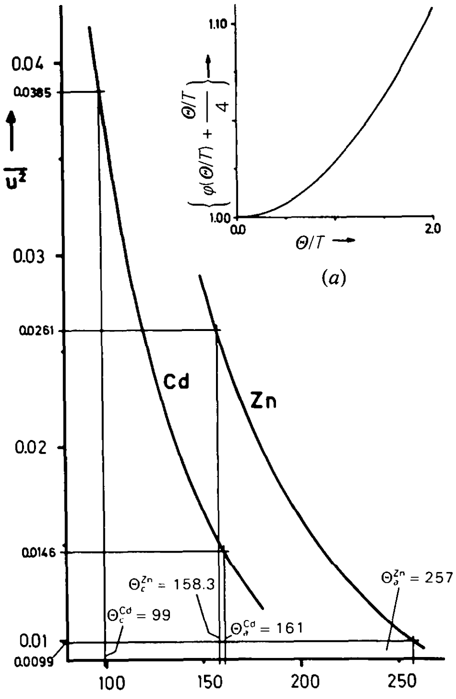
is tabulated by James (1948, p. 219). In Fig. 1 this function is plotted against $\Theta/T$. For high temperatures, $\Theta/T$ is small and the term in parentheses is almost 1.

Thus, at the melting temperature $T_M$

$$\bar{u}_M = \left(\frac{3\hbar^2 T_M}{mk\Theta^2}\right)^{1/2}. \tag{2}$$

If $r$ is the radius of the space occupied by the atom, the ratio $x$ is given by

$$x = \frac{\bar{u}_M}{r} = \left(\frac{3\hbar^2 T_M}{mk\Theta^2 r^2}\right)^{1/2}. \tag{3}$$



(*a*)

(*b*)

Fig. 1. Plots of (*a*) $\left[\varphi\left(\frac{\Theta}{T}\right) + \frac{\Theta/T}{4}\right]$ *vs* $\Theta/T$ and (*b*) $\overline{u^2}$ *vs* $\Theta$.

We should compare this ratio $x$ with the 'Lindemann's melting formula' given by Ziman (1965)

$$x_Z = \left(\frac{9\hbar^2 T_M}{mk\Theta^2 r^2}\right)^{1/2} = \sqrt{3}.x. \tag{4}$$

Ziman states that $x_Z$ seems to be in the range 0·2 to 0·25 in most solids.

It is therefore of interest to examine whether $x_Z$ for Zn and Cd is also about 0·2 and to estimate the ratio $\bar{u}_M/r$. Yamata & Doyama (1972), for instance, applied Lindemann's melting formula (4) to the f.c.c. alloys Cu–Zn, Cu–Al, Ag–Mg, Ag–Zn and Ag–Cd and found a value for $x_Z$ of about 0·2 by using for $r$ the radius of the Wigner–Seitz cell at room temperature. In this paper the radius of the space occupied by each atom is calculated by the relation

$$\frac{4\pi r^3}{3} = \frac{V_{\rm EC}}{N} \rightarrow r = 0{\cdot}4693\,(a_{t_M}^2.c_{t_M})^{1/3}, \tag{5}$$

where $V_{\rm EC} = (\sqrt{3}/2)\,a_{t_M}^2.c_{t_M}$ is the volume of the elementary hexagonal cell and $N$ (= 2 for Zn and Cd) is the number of atoms per unit cell; $a_{t_M}$ and $c_{t_M}$ are the lattice parameters near the melting point. Although the difference in the results of $x$ and $x_Z$ using the room-temperature or melting-point lattice parameters is small, in this paper the lattice parameters near the melting temperature were calculated and used in (5).

Other approaches to Lindemann's law are given, for example, by Shapiro (1970), Singh & Sharma (1968) and Martin & O'Connor (1977).

### Results and discussion

Using the values in Table 1 and interpolating the function

$$\left[\varphi\left(\frac{\Theta}{T}\right) + \frac{\Theta/T}{4}\right]$$

with the help of Fig. 1(*a*), the relation (1) is plotted for Zn and Cd with $T = 293$ K in Fig. 1(*b*).

Values for $\Theta_a$ and $\Theta_c$, estimated in Fig. 1(*b*), together with an average value $\Theta_{\rm av}$ determined by

$$\frac{1}{\Theta_{\rm av}^2} = \frac{1}{3}\left(\frac{1}{\Theta_c^2} + \frac{2}{\Theta_a^2}\right) \tag{6}$$

are collated in Table 2. $x$ and $x_Z$ in Table 2 were calculated using $r$ defined by (5) and $\Theta_{\rm av}$ defined by (6). The result for

Table 1. *The lattice parameters a and c at room temperature, the mean-square vibrational amplitudes* $\overline{u_a^2}$ *and* $\overline{u_c^2}$ *in the* **a** *and* **c** *directions of the lattice* [*values for* Zn *by Rossmanith* (1977), *for* Cd *by Rossmanith* (1978)], *the linear expansion coefficients* $\beta_a$, $\beta_c$ (*Hellwege*, 1967, *p*. 136), *the melting points* $t_M$ (*Lax*, 1967), *the lattice parameters near the melting point* {*calculated with* $a_{t_M} = a[1 + \beta_a(t_M - 20)]$ *and* $c_{t_M} = c[1 + \beta_c(t_M - 20)]$}, *and the absolute atomic mass* {*calculated by* $m$ = *relative mass* × 1·6604 × $10^{-24}$ [*values for relative mass by Lax* (1967)]}

| | $a$ (Å) | $c$ (Å) | $\overline{u_a^2}$ | $\overline{u_c^2}$ | $\beta_a$(×10⁶/°C) | $\beta_c$(×10⁶/°C) | $t_M$(°C) | $a_{t_M}$ (Å) | $c_{t_M}$ (Å) | $m$(×10²⁴) (g) |
|---|---|---|---|---|---|---|---|---|---|---|
| Zn | 2·6659 (1) | 4·9403 (2) | 0·0099 (2) | 0·0261 (2) | 14 | 55 | 419·5 | 2·681 | 5·048 | 108·54 |
| Cd | 2·977 (1) | 5·612 (2) | 0·0146 (3) | 0·0385 (3) | 17 | 49 | 321 | 2·992 | 5·695 | 186·63 |

$x_Z$ agrees with the statement by Ziman, $x_Z$ being in the range 0·2 to 0·25.

It seems that melting begins in both solids if the amplitude of vibration $(\overline{u^2})^{1/2}$ reaches a value of about 12% of the radius of the space occupied by the atom.

The melting parameters considered here have been averaged over all directions of motion, and the observed anisotropy between $\overline{u_c^2}$ and $\overline{u_a^2}$ merits further study.

Table 2. *X-ray Debye temperatures* $\Theta_a$ *and* $\Theta_c$ [*estimated in Fig.* 1(*b*)], *and* $\Theta_{av}$ [*calculated with formula* (6)], *values for r* [*defined in* (5)], *and for x and* $x_Z$ [*defined in* (3) *and* (4)]

| | $\Theta_a$ (K) | $\Theta_c$ (K) | $\Theta_{av}$ (K) | $r$ (Å) | $x$ | $x_Z$ |
|---|---|---|---|---|---|---|
| Zn | 257 | 158·3 | 206·7 | 1·554 | 0·12 | 0·21 |
| Cd | 161 | 99·0 | 129·4 | 1·740 | 0·12 | 0·21 |

## References

HELLWEGE, K. H. (1967). *Einführung in die Festkörperphysik*. Berlin, Heidelberg, New York: Springer.

JAMES, R. W. (1948). *The Crystalline State*. Vol. II. *The Optical Principles of the Diffraction of X-rays*. London: Bell.

LAX, E. (1967). *D'Ans–Lax: Taschenbuch für Chemiker und Physiker*. Band 1. Berlin, Heidelberg: Springer.

MARTIN, C. J. & O'CONNOR, D. A. (1977). *J. Phys. C*, **10**, 3521–3526.

ROSSMANITH, E. (1977). *Acta Cryst.* A**33**, 593–601.

ROSSMANITH, E. (1978). *Acta Cryst.* A**34**, 497–500.

SHAPIRO, J. N. (1970). *Phys. Rev. B*, **1**(10), 3982–3989.

SINGH, A. K. & SHARMA, P. K. (1968). *Can. J. Phys.* **46**, 1677–1679.

YAMATA, R. & DOYAMA, M. (1972). *Phys. Lett. A*, **41**(2), 165–166.

ZIMAN, J. M. (1965). *Principles of the Theory of Solids*. Cambridge Univ. Press.

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## Phase information from anomalous-scattering measurements.

By WAYNE A. HENDRICKSON, *Laboratory for the Structure of Matter, Naval Research Laboratory* 6030, *Washington, DC* 20375, *USA*

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### Abstract

The fundamental basis for alternative expressions for the phase probability distributions related to anomalous-scattering measurements is examined. Exact, general expressions are derived and these are then simplified for the special situations that normally apply in practice.

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North (1965) and Matthews (1966) have described methods for incorporating the phase information from anomalous-scattering measurements into the isomorphous-replacement method in a way that properly takes into account the higher accuracy that is intrinsic to measurements of anomalous differences relative to those of isomorphous differences. These methods have proven to be very effective in protein crystallography. However, uncertainty has persisted as to the correct form for the error function to be used in phase probability distributions. Although North and Matthews formulate the problem somewhat differently, after using similar approximations in their derivations they seemingly arrive at the same result. Yet, varying interpretations have been put forward regarding valid forms for use in practice.

The purpose of this note is to clarify the basic origin of the alternative error expressions and to derive the appropriate expressions without approximation. Expressions that can be cast in the simplified representation of Hendrickson & Lattman (1970) are then seen to be based on an alternative error model rather than on questionable approximations.

Moreover, the exact expressions given here may be required in neutron diffraction where anomalous-scattering effects can be quite large. Expressions appropriate to phase information from anomalous scattering without isomorphous replacement are also given.

An isomorphous-replacement experiment that includes anomalous-scattering measurements presents, for each reflection *hkl*, three observations: the structure amplitude $F_P$ from the native or 'parent' crystal structure and the structure amplitudes $F_{PH}^+$ and $F_{PH}^-$ at *hkl* and its Friedel mate $\bar{h}\bar{k}\bar{l}$

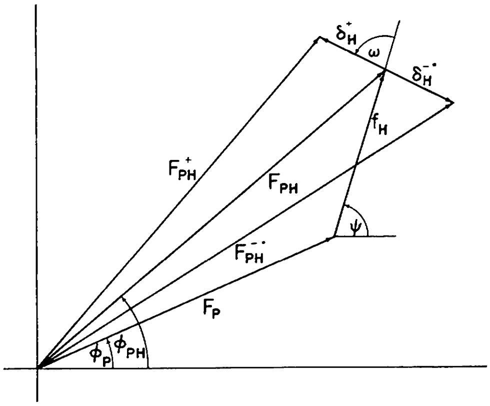

Fig. 1. Vector diagram showing relationships among the structure factors from an isomorphous-replacement experiment that include anomalous-scattering measurements. The vectors denoted $F_{PH}^{-*}$ and $\delta_H^{-*}$ are complex conjugates of structure factors for reflection $\bar{h}\bar{k}\bar{l}$ and all other vectors are structure factors for reflection *hkl*.

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