

## High-Voltage Electron Diffraction Measurement of the Debye Temperatures of Cr, $\alpha$ -Fe and their Disordered Alloys\*

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The critical-voltage effect of high-voltage electron diffraction has been used to measure the X-ray Debye temperatures of Cr,  $\alpha$ -Fe and their disordered alloys. The 220 critical voltages were measured at room and elevated temperatures for the pure metals and at room temperature for five intermediate compositions. The data for the pure metals were sufficient to determine both the Debye temperature and the deviation from the free-atom value of the atomic scattering factor at the first-order reflection position. The results agree with those of other workers. The scattering factor deviations were assumed to be the same in the alloys as in the pure metals, and this made it possible to determine the alloy Debye temperatures from a single room-temperature measurement of the critical voltage at each intermediate composition. The Debye temperatures are analyzed successfully in terms of a simple one-parameter theory, and are correlated with the alloy melting-point data through Lindemann's formula.

### Introduction

When the electron-diffraction pattern from a crystal several thousand angströms in thickness is studied at electron accelerating voltages greater than about 100 kV, one often finds a critical voltage at which the second-order Kikuchi line associated with a set of atomic planes vanishes, and above and below which the asymmetry of the excess-deficiency profile of the center line of the Kikuchi pattern is reversed (Watanabe, Uyeda & Kogiso, 1968). The value of the critical voltage depends on values of the average atomic scattering factors at the reciprocal-lattice positions corresponding to the set of atomic planes (the systematic reflections). The average atomic scattering factors for an alloy depend on the free-atom atomic scattering factors modified to take account of the following: (1) redistribution of the outer electrons of the atoms in the crystal-line environment (this may modify the free-atom atomic scattering factor at low-order reflections; usually only the value at the first-order reflection is significantly modified), (2) composition and long-range order, and (3) mean-square static and thermal displacements of atoms from average lattice sites which cause a Debye-Waller type of attenuation of the scattering factors. To utilize the critical-voltage effect one must employ an appropriate model which characterizes all or some of the above effects by a few well chosen parameters. Some of these parameters may be fixed beforehand

(*e.g.* composition by chemical analysis, or long-range order by heat treatment), and others may be determined from values of critical voltages. Just what critical-voltage measurements are needed (*e.g.* for different systematics, at various temperatures and/or compositions) depends on which parameters are regarded as undetermined. For a review of the applications of the critical voltage effect, see Lally, Humphreys, Methereil & Fisher (1972).

The information which critical-voltage measurements give is essentially the same as can be obtained from X-ray diffraction measurement of Bragg intensities. However, the electron-diffraction method has the advantage of probing microscopic volumes 1  $\mu$ m or less in diameter and several tenths of a micron in thickness. It is also possible to use the direct imaging facility to examine the microstructure of the region. This makes specimen preparation much less critical than for a comparable X-ray study.

The present paper reports measurements of the 220 critical voltages of Cr and  $\alpha$ -Fe (both b.c.c.) at room and elevated temperatures, and of five intermediate alloys at room temperature. The data for the pure metals is sufficient to determine the X-ray Debye temperatures,  $\theta_M$ , and the values of the atomic scattering factors at the first-order reflections. Because the atomic scattering factors for atoms in the alloys are assumed to be the same as for atoms in the pure metals, and because the static mean-square displacements due to the atomic radius disparity between Cr and Fe can be shown to be negligible in these alloys, it is possible to find the alloy Debye temperatures by a single room-temperature critical-voltage measurement at each intermediate composition.

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### Experimental

The alloys were prepared by melting together 99.99% Fe and 99.99% Cr in a vacuum furnace. After being rolled into thin sheets in the usual manner, the alloys were annealed at 1000°C for several hours and quenched. Compositions were determined to 0.1% by chemical analysis. Thin foils were obtained from the sheets by conventional electropolishing.

The critical voltages were determined by observing the 220 Kikuchi line and the asymmetry of the middle line in selected-area diffraction patterns at various voltages. The experimental critical voltages and temperatures are given in Table 1.

Table 1. *Experimental compositions, temperatures, and critical voltages, and the room-temperature X-ray Debye temperatures deduced from them*

Mole fraction of Cr	Temperature (K)	Critical voltage (kV)	$\theta_M$ (K)
0.000	295 ± 2	305 ± 3	424 ± 12
0.000	568 ± 5	254 ± 3	—
0.212	295 ± 2	293 ± 3	422 ± 12
0.325	295 ± 2	285 ± 3	418 ± 12
0.478	295 ± 2	277 ± 3	420 ± 12
0.763	295 ± 2	271 ± 3	459.5 ± 12
0.859	295 ± 2	267 ± 3	466 ± 12
1.000	295 ± 2	265 ± 3	495 ± 12
1.000	658 ± 5	215 ± 3	—

### Analysis of data

Assuming that each atomic site is statistically cubic, and that the mean-square displacement has a Gaussian distribution, the potential distribution of each atom is convoluted with a spherically symmetrical 'spread function' the half-width of which depends on the identity of the atom. Thus, each atomic scattering factor is multiplied by a Gaussian of appropriate half-width, and the average atomic scattering factor is

$$f = m_A f_A \exp(-M_A) + m_B f_B \exp(-M_B), \quad (1)$$

where

$$M_A = (k^2/6) \langle u^2 \rangle_A, \quad (2)$$

and similarly for  $M_B$ . In these equations  $m_A$  is the mole fraction of  $A$  atoms,  $f_A$  is the atomic scattering factor of an  $A$  atom in the crystal,  $\langle u^2 \rangle_A$  is the mean-square displacement of  $A$  atoms, and  $k = 4\pi s$ , where  $s = (\sin \theta)/\lambda$ . It is useful to express  $\langle u^2 \rangle_A$  and  $\langle u^2 \rangle_B$  in terms of correlation functions which have been studied elsewhere (Shirley, 1974a). Let  $\sigma_i^A = (1, 0)$  for an  $(A, B)$  atom at site  $i$ . Then

$$\langle u^2 \rangle_A = \sum_i \sigma_i^A u_i^2 / \sum_i \sigma_i^A = \langle \sigma^A u^2 \rangle / m_A,$$

where the sums are over all lattice sites. Now express  $\sigma_i^A$  (and  $\sigma_i^B$ ) in terms of a new variable  $\sigma_i$  which has the value  $(2m_B, -2m_A)$  for an  $(A, B)$  atom at site  $i$ .

This variable has the property  $\langle \sigma_i \rangle = 0$ . Then one has  $\sigma_i^A = m_A + \frac{1}{2}\sigma_i$  and

$$\langle u^2 \rangle_A = \langle u^2 \rangle + (2m_A)^{-1} \langle \sigma u^2 \rangle, \quad (3a)$$

and similarly

$$\langle u^2 \rangle_B = \langle u^2 \rangle - (2m_B)^{-1} \langle \sigma u^2 \rangle. \quad (3b)$$

From equations (3), equation (1) may be written

$$f = \exp(-M) [m_A f_A \exp(-\Delta M_A) + m_B f_B \exp(-\Delta M_B)] \quad (4)$$

where

$$M = (k^2/6) \langle u^2 \rangle, \quad (5a)$$

$$\Delta M_A = (k^2/12m_A) \langle \sigma u^2 \rangle, \quad (5b)$$

$$\Delta M_B = -(k^2/12m_B) \langle \sigma u^2 \rangle. \quad (5c)$$

In general  $\langle u^2 \rangle$  contains a temperature-independent part attributable to the static distortion of the lattice arising from the atomic-radius disparity between the two types of atoms, and it contains a temperature-dependent part attributable to thermal vibration [see, for example, Shirley (1974a)]. Coyle & Gale (1955) give a formula for the static mean-square displacement, which in simplified form is

$$\langle u^2 \rangle(\text{static}) = 0.36 m_A m_B (a_A - a_B)^2$$

where  $a_A$  is the lattice parameter of the pure  $A$  metal. For Cr-Fe alloys the maximum value of  $\langle u^2 \rangle$  (static) is therefore about  $4 \times 10^{-5} \text{ \AA}^2$ . This compares with an error in  $\langle u^2 \rangle$  of  $\pm 7.5 \times 10^{-4} \text{ \AA}^2$  corresponding to the error of  $\pm 3$  kV in the measured critical voltage. The only appreciable contribution to  $\langle u^2 \rangle$  is therefore from thermal vibrations and  $\langle u^2 \rangle$  may be represented by the well-known form (James, 1962)

$$\langle u^2 \rangle = 436.64 \left\{ \frac{T\varphi(\theta_M/T)}{\mu\theta_M^2} + \frac{1}{4\mu\theta_M} \right\} (\text{\AA}^2) \quad (6)$$

where  $\mu = m_A \mu_A + m_B \mu_B$ , and  $\mu_A$  is the atomic weight of an  $A$  atom,  $T$  is the temperature of the crystal, and  $\varphi$  is Debye's function. In a crystal for which the atomic-radius disparity is negligible, the analysis of Shirley (1974a) [specialize equation (24) of this reference by setting all terms with coefficient  $\gamma$  or  $\gamma^2$  ( $\gamma$  is a measure of the order in atomic radius disparity) to zero, and set  $l=0$ ] shows that, in the classical regime,

$$\langle Ju_0^2 \rangle = \kappa T \langle J \rangle \text{Trace } \mathbf{G}_{00}, \quad (7)$$

where  $\kappa$  is Boltzmann's constant, the subscript 0 refers to an arbitrary origin site,  $J$  is an arbitrary function of all of the  $\sigma$ 's and where

$$\mathbf{G}_{00} = v_k^{-1} \int d^3\mathbf{k} \varphi^{-1}(\mathbf{k})$$

in which  $\varphi(\mathbf{k})$  is the Fourier transform of the  $3 \times 3$  force-constant matrix appropriate to the average interatomic potential, and where the integration is over a Brillouin zone of volume  $v_k$ . If  $J=1$  in (7) we obtain the classical equivalent of (6), and if  $J=\sigma_0$  we find

$\langle \sigma_0 u_0^2 \rangle = 0$  because  $\langle \sigma_0 \rangle = 0$ . Thus, if the atomic-radius disparity is negligible, then  $\langle \sigma u^2 \rangle$  in equations (5) is negligible. Hence the appropriate model for the disordered Cr-Fe alloys is one in which the average atomic scattering factor is given by

$$f = \exp(-M) \bar{f} \quad (8)$$

where  $\bar{f} = m_A f_A + m_B f_B$ , and where  $\langle u^2 \rangle$  is given by equation (6).

The critical voltage occurs when branches 2 and 3 [in the notation of Humphreys & Fisher (1971)] of the dispersion surfaces come into contact at a symmetry point (Nagata & Fukuhara, 1967; Metherell & Fisher, 1969). The  $n$ -beam matrix diagonalization method of Fisher (1968) was employed in a computer program which locates the voltage for which dispersion surfaces 2 and 3 coincide for a given  $f$ . For the pure metals the scattering factors at all systematic reflections except the first-order were given free-atom values (Doyle & Turner, 1968). The first-order scattering factors were adjusted until  $\langle u^2 \rangle$  obtained from the critical-voltage program gave the same Debye temperature at both room and elevated temperatures when equation (6) was used. The Debye temperatures and scattering factors obtained this way are given in Table 2, where they are seen to compare favorably with the results of independent determinations. Two small corrections for thermal expansion causing a total change of  $3^\circ$  or so in  $\theta_M$  were made. First, in order to evaluate the atomic scattering factors and the Debye-Waller factor at the correct positions in reciprocal space, the correct high-temperature lattice parameters were used in the critical-voltage computer program. Second, thermal expansion causes a weakening of the interatomic force constants so that  $\langle u^2 \rangle$  increases faster with temperature than it would in the absence of anharmonic effects. Multiplication by  $(1 + 2\beta\gamma\Delta T)^{-1}$  of the value of  $\langle u^2 \rangle$  obtained from the critical-voltage computer program corrects for this effect.  $\beta$  is the coefficient of linear expansion,  $\gamma$  is the Grüneisen parameter, and  $\Delta T$  is the difference between the high temperature and room temperature. As a consequence of this correction, the values obtained for  $\theta_M$  are appropriate to room temperature. For the alloys, the first-order scattering factors obtained for the pure metals were assumed, and the scattering factors at all higher-order reflections

were given free-atom values.  $\bar{f}$  was computed using these atomic scattering factors, and the value of  $\langle u^2 \rangle$  deduced from the room-temperature critical voltage was used to deduce  $\theta_M$  from equation (6). The results appear in the right-hand column of Table 1, and they are plotted in Fig. 1.

The errors in the Debye temperatures are based on the errors in the observed critical voltages and temperatures, but not on possible errors in the scattering factors. Errors in  $\bar{f}(110)$  could cause a further systematic shift of all points together in Fig. 1 by as much as  $\pm 15^\circ\text{K}$ ; however the good agreement of the pure-metal Debye temperatures with those of other workers (Table 2) seems to indicate that the systematic errors are considerably less than this.

### Interpretation of results

Recently, Shirley (1974b) rederived the Debye temperature interpolation formula of Mitra & Chattopadhyay (1972), expressing it differently and including the effect of short-range order. The formula is

$$\mu\theta^2 = m_A\mu_A\theta_A^2 + m_B\mu_B\theta_B^2 + (\tau - 1)(1 - \alpha)m_A m_B (\mu_A\theta_A^2 + \mu_B\theta_B^2) \quad (9)$$

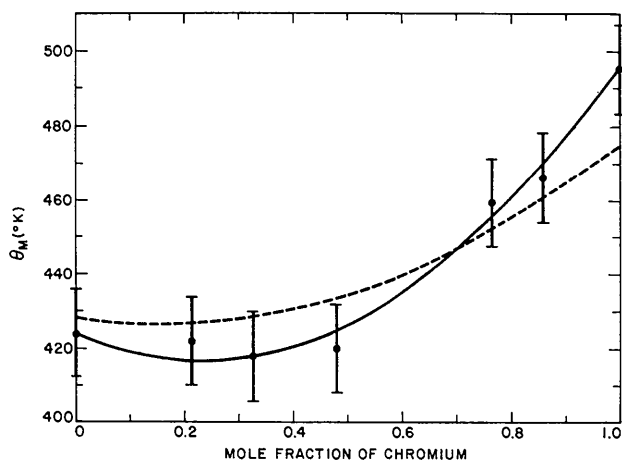


Fig. 1. Variation of the Debye temperature of the Cr-Fe alloys with composition. The solid curve is the best fit of equation (9) to the data ( $\tau=0.72$ ). The broken curve is the best fit of Lindemann's formula, equation (10) ( $x=0.197$ ).

Table 2. X-ray Debye temperatures and atomic scattering factors for Cr and Fe from the present study and from other work

	Cr	Fe
$f(110)$ (present)	$3.040 \pm 0.015$	$3.008 \pm 0.015$
$f(110)$ (other)	$3.067 \pm 0.047$ (1)	$3.012 \pm 0.043$ (2)
$f(110)$ (free-atom)	2.91 (3)	2.97 (3)
$\theta_M$ (present)	$495 \pm 12$	$424 \pm 12$
$\theta_M$ (other: X-ray)	$510 \pm 6$ (4)	$435 \pm 6$ (4)
$\theta_M$ (other: specific heat*)	$505 \pm 6$ (5)	431 (6)

References (in parentheses after the data entries): (1) Fujimoto, Terasaki & Watanabe (1972). (2) Watanabe, Uyeda & Fukuhara (1969). (3) Doyle & Turner (1968). (4) Paakkari (1974). (5) Clusius & Franzosini (1962). (6) Kushwaha (1974).

\* The specific-heat Debye temperatures,  $\theta_D$ , were converted to  $\theta_M$  using the correction due to Zener & Bilinsky (1936).

where  $\theta$  is the alloy Debye temperature,  $\theta_A$  is the Debye temperature of the pure  $A$  metal,  $\alpha$  is the nearest-neighbor Cowley–Warren short-range order parameter (Cowley, 1950), and where the deviation of  $\tau$  from unity is a measure of the factor by which the nearest-neighbor spring constant connecting dissimilar atoms differs from the arithmetic mean of the spring constants connecting similar atoms, *i.e.*  $g_{AB} = \tau(g_{AA} + g_{BB})/2$ , where  $g_{AA}$ , *etc.* are the spring constants. It is theoretically anticipated, and experimentally confirmed for several systems with small atomic-radius disparity, that  $\tau$  is composition-independent. Note also that equation (9) applies to either X-ray or specific heat Debye temperatures provided Poisson's ratio does not vary greatly with composition. This is usually the case.

Equation (9) was fitted to the results by constraining the formula to give the pure-metal Debye temperatures exactly and then choosing  $\tau$  to give a least-squares best fit to the results at intermediate compositions, assuming  $\alpha=0$ . The curve is given in Fig. 1, and it shows that the results are adequately described by a one-parameter model. The value of  $\tau$  is 0.72.

It is enlightening to correlate the results obtained here with another physical property of the alloy system. Yamamoto & Doyama (1972) showed that Lindemann's rule is valid for the  $\alpha$  phase of certain alloys. For the special case of b.c.c. alloys Lindemann's formula (see Ziman, 1969) is written

$$\theta_D = \frac{1}{x} \left( \frac{1800T_m}{\mu a^2} \right)^{1/2} \quad (10)$$

where  $T_m$  is the melting point,  $a$  is the lattice parameter in Å, and  $x$  is dimensionless and constant at 0.2 to 0.25 for most solids.  $x$  is the atomic r.m.s. amplitude at the melting point expressed as a fraction of the Wigner–Seitz radius. In using equation (10),  $T_m$  was the average of the liquidus and solidus temperatures, and the difference between X-ray and specific heat Debye temperatures was ignored. When the melting-point data in Hansen (1958) were used and  $x$  was chosen such that  $\theta_D$  from equation (10) fitted the data best in a least-squares sense,  $x=0.197$  was found. This is in good agreement with what Yamamoto & Doyama (1972) found for the f.c.c. alloys they studied. The

prediction of equation (10) for this value of  $x$  is plotted in Fig. 1, and good agreement is apparent.

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