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Acoustic and optical Debye temperatures of the vitreous system $CoO–Co_2O_3–P_2O_5$

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For the Co–P–O glass system, data have been assembled on acoustic Debye temperatures obtained from ultrasonic wave-velocity measurements, acoustic and optical Debye temperatures determined from infrared absorption studies, and optical Debye temperatures obtained from electrical conductivity measurements. It is argued that these quantities are systematically related in theory, and the relationships are substantiated by the experimental data.

1. Introduction

It is well known that from acoustic wave compressional and shear wave velocities, a characteristic temperature related to the acoustic phonon spectrum of the lattice can be computed. In the theory of conduction processes in amorphous solids, another characteristic temperature related to some average optical phonon frequency is defined [1]. Since the optical and acoustical branches of a lattice vibrational spectrum are interdependent, a systematic relationship should exist between acoustically and electrically determined characteristic temperatures, and moreover temperatures corresponding to both ought to be identifiable in the infrared adsorption spectra of amorphous materials. In spite of the wealth of electrical, optical and acoustic measurements made on vitreous systems, the correlations between these properties as implied above have not yet been seriously tested. One reason why this has not been possible is that, particularly with electrical measurements, it is rare to find requisite data covering a substantial (if not total) compositional range for any one vitreous system. We have measured ultrasonically determined Debye temperatures [2] and infrared absorption [3] over the entire vitreous range of the Co–P–O system that can be obtained by melting cobalt oxides with P_2O_5 in open crucibles. In addition, literature exists on the temperature dependence of the electrical conductivity of a part of this vitreous system (38 to 60 mol % CoO) [4, 5]. So in this case there is sufficient information for an effective discussion on characteristic temperatures to be made, although it would have been better to have available electrical data on glasses with a lower cobalt content as well. A complete discussion of the preparation and chemical composition of the glass system, with data on the composition deendence of the Co^{2+}/Co^{3+} ratio, is given elsewhere [6].

2. General theoretical considerations

The lattice vibrational spectrum of a perfect crystal with P atoms per unit cell consists of three acoustic phonon branches and $(3P - 3)$ optical phonon branches, in each case with phonon wave-vectors K spanning a quasi-continuous spectrum from zero up to a cut-off value (reciprocal lattice vector) when the Brillouin zone boundary is reached. Associated with each optical branch is a quasi-continuous spectrum of phonon frequencies with an upper limiting frequency ν_o^U which occurs when $K = 0$ and a lower limiting frequency ν_o^L when K is at the zone boundary. These optical phonon branches give rise to optical absorption bands centred round the upper limiting frequencies, all of which lie essentially in the infrared region. For the acoustic phonon branches there is also a quasi-continuous spectrum of phonon frequencies with a lower limiting frequency (corresponding to $K = 0$) of zero and with upper limiting frequencies ν_a^U (K at a zone boundary) lying somewhat below the lower limiting frequencies ν_o^L of the optical branches, although for monoatomic lattices these two sets of limiting frequencies actually coincide.

The three sets of limiting frequencies designated by ν_o^U, ν_o^L and ν_a^U (Fig. 1) are systematically related to each other since they are all functions of the cation–anion force constants and the cation and anion masses. However, only in simple idealized cases (e.g. a linear diatomic chain) have these relationships been worked out. Experimentally, however, they ought to be identifiable from the infrared absorption spectrum of the material. Thus presumably the highest value of ν_o^U could be identified with the upper limit of the experimental infrared absorption spectrum, whilst the lowest value of ν_a^U would be associated with the lowest limit of the infrared absorption spectrum (assuming that the spectrum was uncomplicated by overlapping bands, absorption lines originating from molecular degrees of freedom, dangling bonds, or atomic energy-level splitting). Now if we regard the network vibrational spectrum of a glassy material as essentially a diffuse version of the lattice spectrum of the nearest equivalent crystal, the above picture remains essentially unchanged. In other words the concept of limiting frequencies still remains, though there will be a broadening and increased overlapping of infrared absorption bands.

Now in the Debye continuum approximation for

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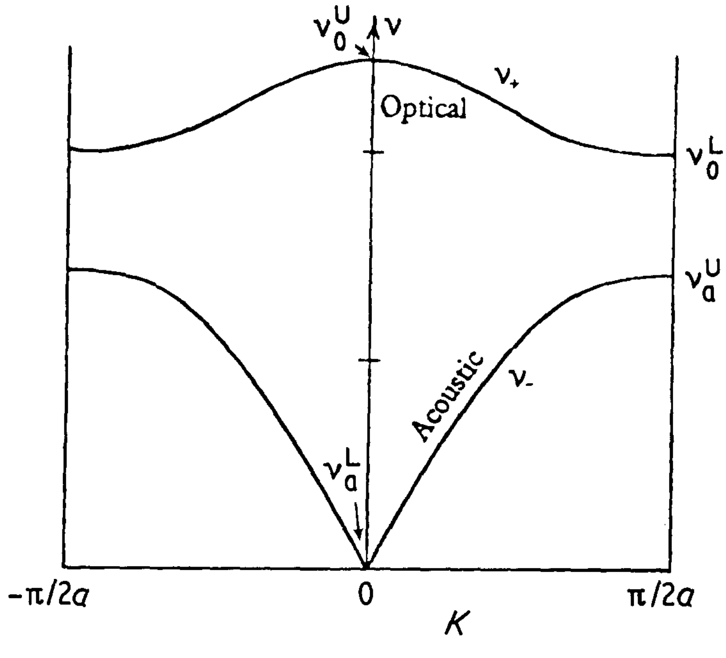

Figure 1 Schematic diagram of the dispersion relationships for optical and acoustic phonon modes in a vibrating lattice. For a perfect crystal with P atoms per unit cell there are (3P − 3) optical modes with different ν_o^U and ν_o^L values and three acoustic modes with different ν_a^L and ν_a^U values (excluding degeneracy).

phonon states there is defined a parameter

$$\Theta = h\nu_a/k \qquad (1)$$

where h is Planck's constant and k is Boltzmann's constant, Θ is the Debye temperature and ν_a is an upper cutoff frequency called the Debye frequency which is to be roughly associated with values of ν_a^U, i.e. ν_a is some kind of average over the upper limiting frequencies for the acoustic phonon modes occurring in a real crystal lattice. As will be shown later, Θ may (with certain assumptions) be expressed as a function of the ultrasonic wave velocities in the material (presumably isotropic). In the polaron model of hopping conduction in amorphous materials another parameter

$$\theta_D = h\nu_o/k \qquad (2)$$

arises where ν_o is defined as an average optical phonon frequency, i.e. ν_o is some kind of average over all ν_o^U and ν_o^L values; since $(\nu_o^U - \nu_o^L)$ is small compared with either frequency limit, then $\nu_o \approx \nu_o^{-U} \approx \nu_o^{-L}$. Now since we have argued previously that ν_o^U, ν_o^L and ν_a^U values are systematically related, one might reasonably expect that Θ and θ_D exhibit a systematic relationship. Therefore, a main purpose of this paper is to see if, for Co–P–O glasses, there is any correlation between the compositional dependence of θ_D as determined from electrical conductivity measurements, and Θ as determined from ultrasonic measurements. At the same time we intend to see whether quantities resembling Θ and θ_D can be identified in our infrared spectra.

3. Debye continuum of phonon states: expression for Debye temperature as a function of ultrasonic wave velocities

In the Debye continuum model it is assumed that the acoustic phonon spectrum is spatially isotropic and that the number of phonon states per unit volume in the frequency range ν to $(\nu + d\nu)$ is given by $g(\nu)d\nu$ where

$$g(\nu) = 4\pi\nu^2\left(\frac{1}{c_L^3} + \frac{2}{c_T^3}\right) \qquad 0 \leqslant \nu \leqslant \nu_a$$

$$g(\nu) = 0 \qquad \nu > \nu_a \qquad (3)$$

Here the first term is associated with a longitudinal phonon branch assumed to have a constant velocity c_L and the second term is associated with two transverse phonon branches (with orthogonal direction of polarization) assumed to have constant velocity c_T. Furthermore the total number of phonon states is assumed to be $3N$ where N is the number of atoms per unit volume, so that from the relation $\int_0^\infty g(\nu)d\nu = 3N$, and Equations 1 and 3, we find that

$$\nu_a^3 = \frac{9N}{4M}\left(\frac{1}{c_L^3} + \frac{2}{c_T^3}\right) \qquad (4)$$

so that

$$\Theta_{el} = \frac{h}{k}\nu_a = \frac{h}{k}\left(\frac{3\varrho N_a P}{4\pi M}\right)^{1/3}\left(\frac{(1/c_L^3) + (2/c_T^3)}{3}\right)^{1/3} \qquad (5)$$

where ϱ is the density, N_a is Avogadro's number, P is the number of atoms in the chemical formula, Θ_{el} denotes the Debye temperature determined by acoustic phonon velocities and M is the molecular weight.

In its application to crystals, the model is equivalent to the assumptions that (i) the Brillouin zone, which limits the range of allowed values of K, can be replaced by a sphere of the same volume in reciprocal space, and (ii) there is zero dispersion, i.e. the velocities of longitudinal and transverse photons are constant. Clearly a value of Θ_{el} for a given crystal or glass can readily be calculated from ultrasonic wave measurements on isotropic specimens (polycrystal or glass). A Debye temperature Θ_H can also be determined by attempting to fit empirically the temperature dependence of the experimental heat capacity of a material to the curve predicted by the Debye continuum model of lattice heat capacity.

TABLE I Characteristic (Debye) temperatures calculated from ultrasonic measurements, conductivity measurements and infrared spectrum for Co–P–O glasses

Glass*	($CoO + Co_2O_5$) (mol %)†	Debye temperature		Optical Debye temperature	
		Θ_{el} (calculated from ultrasonic measurements)	Θ_{IR} (calculated from IR using $\bar{\nu}_{IR}$)	$(\theta_D)_{IR}$ (calculated from IR using ν_{IR}^{U})	θ_D (conductivity measurements)
C-1	4.05	305	263	585	
C-3	5.19	340	263	585	
C-5	6.02	375	263	585	
C-8	6.61	385	270	600	
C-9	7.14	393	270	600	
C-15	15.61	403	270	600	
C-19	24.39	397	267	594	
C-22	37.63	388			820
C-24	40.17	387	285	630	
C-27	43.8	386	300	660	844
C-32	47.37	386	308	675	870
C-38	54.64	391			893
C-42	57.78	398	345	750	
C-45	59.21	407	360	780	939

*The glass labels C-1 to C-45 are given to permit cross-reference to other work, published and to be published.

†Glass numbers C-22, C-27, C-32 and C-45 correspond respectively to glass numbers 25 75, 30 70, 40 60, 50 50 and 60 40, in Basha [4] and Hogarth and Basha [5]. In those reference sources the quoted mole percentages of CoO are starting compositions prior to melting, whereas data given the second column above refer to final compositions subsequently obtained by the analytical procedures described by Higazy and Bridge [2].

It is found that for many simple crystalline solids Θ_H agrees with Θ_{el} remarkably well (to within a few per cent). When amorphous materials are considered there are fewer experimental data to be discussed (only silica seems to have been examined in detail), but the picture would appear to be much less satisfactory. At temperatures $\gtrsim 25$ K the heat capacities of vitreous silica and quartz crystal are virtually identical and can be explained by Debye theory, i.e. the Debye temperature as defined above remains a meaningful concept for this temperature range, but at lower temperatures the heat capacity of vitreous silica becomes greater than that of the crystal analogue by several orders of magnitude. This effect is particularly strange when we consider that at temperatures approaching 0 K the Debye continuum theory ought to work particularly well (and indeed this is so for crystals), because only very long wavelengths (i.e. $K \to 0$) are excited at such low temperatures. The origin of this effect has been formally proposed to be the same as the origin of the lower-temperature acoustic loss in two-level and two-well systems. However, we are presently concerned only with properties (electrical and ultrasonic) at relatively high temperatures for which the concept of a Debye temperature does appear to be applicable to amorphous material.

4. Polaron model of conductivity in non-crystalline solids

Mott [7] has discussed the conduction process in terms of hopping between localized states and has proposed an expression for the conductivity of the form

$$\sigma = (F_o Ne^2 a^2/kT)\, c(1 - c)\, e^{-2\alpha a}\, e^{-\omega/kT} \qquad (6)$$

where a is the site spacing, N is the number of sites or transition-metal ions per unit volume, c is the fraction of sites occupied by an electron and therefore in the low-valence state, F_o is a jump frequency, α is a tunnelling probability, T is the absolute temperature and ω is the activation energy for conduction.

Assuming that a strong electron–lattice interaction exists, the activation energy ω is the result of polaron formation with binding energy ω_H and any energy difference ω_D which might exist between the initial and final sites due to variations in the local arrangements of ions. Austin and Mott [1] show that

$$\left.\begin{array}{lll} \omega = \omega_H + \frac{1}{2}\omega_D & & \text{for } T > \frac{1}{2}\,\theta_D \\ \omega = \omega_D & & \text{for } T < \frac{1}{4}\,\theta_D \end{array}\right\} \qquad (7)$$

where θ_D, defined by $\hbar\omega = k\theta_D$, is a temperture characteristic of the average optical-phonon frequency. A detailed theory of this temperature dependence applicable to phosphate glasses has been given by Schnakenberg [8].

Historically the above equation was developed to explain the observed conduction processes in chalcogenide glasses. More recently several workers have shown that the conduction behaviour of a number of phosphate glasses [4, 5, 9–12], including our Co–P–O system, is consistent with the above model.

It is apparent from Equations 6 and 7 that the polaron model predicts that an appreciable departure from a linear log σ against $1/T$ plot should occur below a temperature of $\frac{1}{2}\theta_D$ where θ_D is given by extrapolation of the linear part of the log σ against $1/T$ curve to meet the $1/T$ axis at a temperature of $\approx \frac{1}{2}\theta_D$. Some workers have called θ_D the optical Debye temperature, presumably because it defines a boundary temperature between two different kinds of temperature dependence of conductivity.

5. Discussion of results

In Table I we give for Co–P–O glasses the Debye temperature Θ_{el} calculated from ultrasonic measurements [2], and the optical Debye temperature computed from electrical conductivity data [4, 5]. The

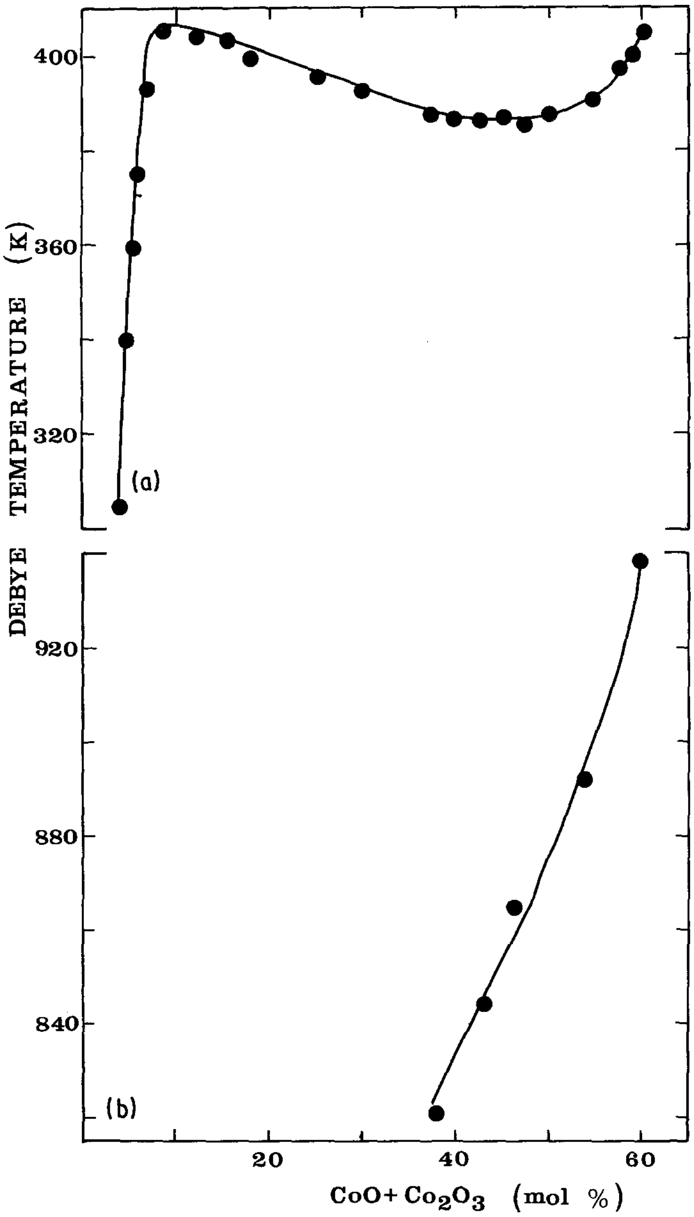

Figure 2 Variation of Debye temperature with composition for the Co–P–O glasses: (a) Debye temperature Θ_{el} calculated from ultrasonic measurements, (b) optical Debye temperature θ_D calculated from electrical conductivity data.

compositional dependence of these quantities is also plotted in Fig. 2. Electrical conductivity data were available only for glasses of CoO oxide content exceeding 38 mol %. However, over the limited range in which comparison is thus possible it will be observed that θ_D correlates closely with Θ, i.e.

$$\Theta_{el} \approx \theta_D/2 \qquad (8)$$

for all the glass compositions. We will now show that this ratio can be readily understood theoretically by considering our glasses as an assembly of linear diatomic chains of the type –O–Co–O–Co– and –O–P–O–P–. For the diatomic chain the theoretical values of the limiting phonon frequencies are given simply [13] by

$$\begin{aligned} \nu_o^U &= 2C\left(\frac{1}{M_1} + \frac{1}{M_2}\right)^{1/2} \\ \nu_o^L &= \left(\frac{2C}{M_2}\right)^{1/2} \\ \nu_a^U &= \left(\frac{2C}{M_1}\right)^{1/2} \end{aligned} \qquad (9)$$

where M_1 and M_2 are the cation and anion masses ($M_1 > M_2$), and C is the anion–cation force constant. Let us now assume that

$$\begin{aligned} (\nu_o^U + \nu_o^L)/2 &\approx \theta_D \\ \nu_a^U &\approx \Theta_{el} \end{aligned} \qquad (10)$$

Thus we find that for –O–Co–O–Co– chains

$$\frac{\theta_D}{\Theta_{el}} \approx 2.13 \qquad (11)$$

and for –O–P–O–P– chains

$$\frac{\theta_D}{\Theta_{el}} \approx 2.23 \qquad (12)$$

Note that the ratio thus tends to increase slowly with CoO content, which is exactly what we observed experimentally.

We now discuss the possibility of identifying quantities corresponding to Θ_{el} and θ_D in our infrared spectrum [3]. Using the upper frequency limit ν_{IR}^U of the absorption band in our glasses (see Fig. 3), we

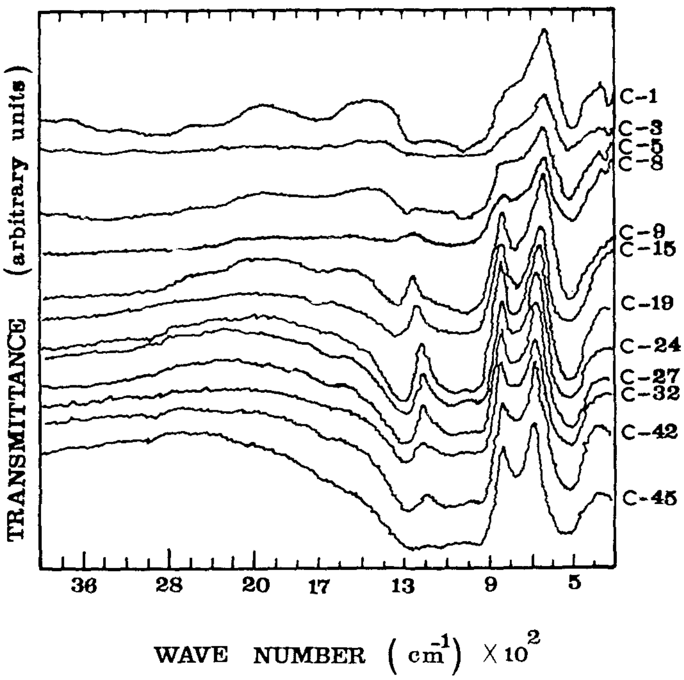

Figure 3 Infrared spectra of some Co–P–O glasses. In Hogarth and Basha [5] (which contains data on additional glasses) these curves are plotted on an enlarged scale to allow accurate evaluation of $(\theta_D)_{IR}$ and Θ_{IR} and permit the identification of individual bands. Glass labels C-1 to C-45 refer to total cobalt oxide contents (CoO + Co_2O_3) which are respectively 4.05, 5.19, 6.02, 6.61, 7.14, 15.61, 24.4, 40.2, 43.8, 47.4, 57.8, 59.2 %, (after Higazy and Bridge [3]).

have computed (Table I) a quantity

$$(\theta_D)_{IR} = \frac{h\nu_{IR}^U}{k} \tag{13}$$

which appears to be in excellent agreement with the few θ_D values computed from conductivity measurements that are available. Further, the compositional dependence of $(\theta_D)_{IR}$ is seen (Fig. 4) to be of the same form as that of Θ, i.e.

$$\frac{(\Theta_D)_{IR}}{\Theta_{el}} \approx 2 \tag{14}$$

for the entire compositional range of our Co–P–O glasses. Finally, according to Sherwood [14] the "centre frequency" of the infrared absorption band, as defined by Plendl [15, 16], i.e.

$$\nu_{ctr} = \frac{\int_{\nu_1}^{\nu_2} \nu f(\nu)\,d\nu}{\int_{\nu_1}^{\nu_2} f(\nu)\,d\nu} \tag{15}$$

where $f(\nu)$ = reflectivity or absorption coefficient, should be in close agreement with the quantity ν_a occurring in Debye's continuum theory. For present purposes we have assumed that

$$\nu_{ctr} \approx \bar{\nu}_{IR} = (\nu_{IR}^U + \nu_{IR}^L)/2 \tag{16}$$

The corresponding temperature $\Theta_{IR} = (h/k)\bar{\nu}_{IR}$ is seen (Fig. 5) to be in good agreement with Θ_{el}, i.e. over the entire compositional range Θ_{IR}/Θ_{el} varies only from 0.7 to 0.9.

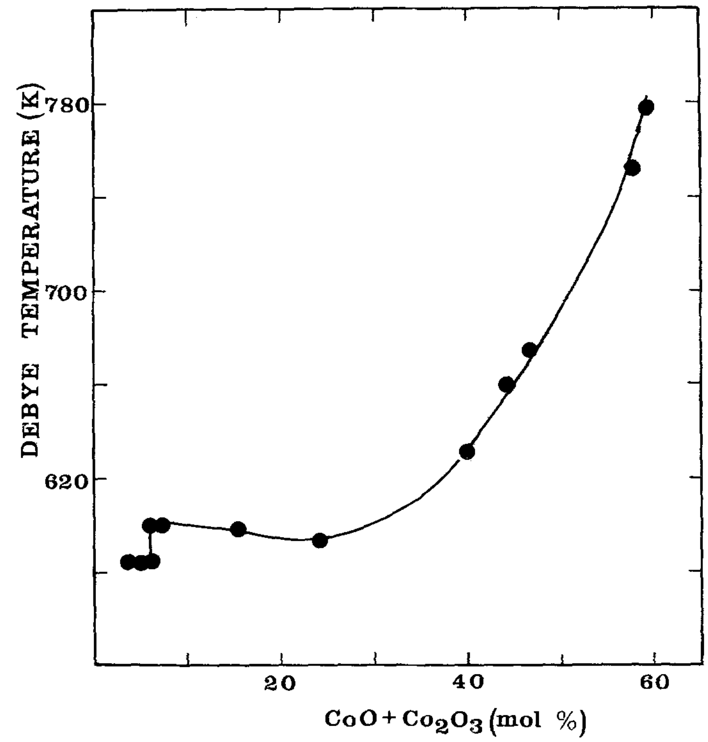

Figure 4 Compositional dependence of optical Debye temperature $(\theta_D)_{IR}$, calculated from infrared spectra of Co–P–O glasses using the upper frequency limit ν_{IR}^U of the absorption bands.

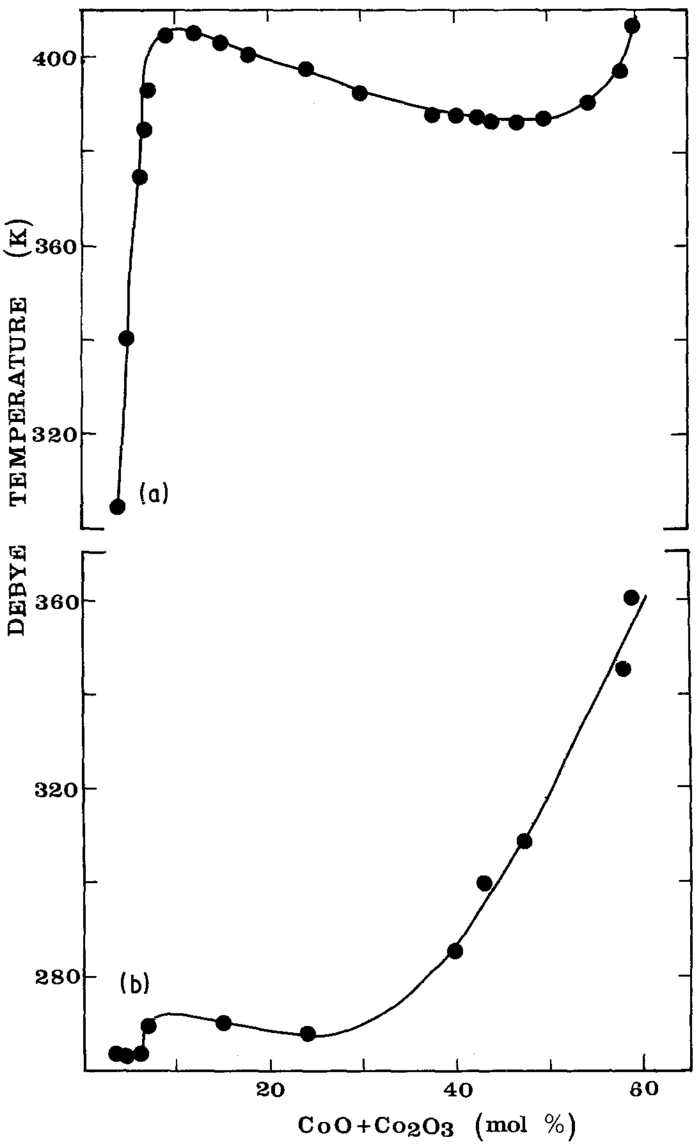

Figure 5 Variation of Debye temperature with composition in Co–P–O glasses: (a) Debye temperature Θ_{el} calculated from ultrasonic measurements, (b) Debye temperature Θ_{IR} calculated from the average frequency $\bar{\nu}_{IR}$ using the upper and lower frequency limits of absorption bands in the Co–P–O glasses.

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