CRYSTALLOGRAPHIC DATA OF 8-METHOXY PSORALEN

As a part of the programme to study crystal structure and conformation of some simple drugs, we have undertaken structure analysis of 8-methoxy Psoralen ($C_{12}H_8O_4$). Thin platy needle-shaped crystals of 8-methoxy Psoralen were crystallised from C_6H_6 petroleum ether solution. Small single crystals were chosen for goniometric and X-ray examination. Rotations, oscillation and Weissenberg photographs showed that the substance is orthorhombic.

The density of the substance as measured pycnometrically by taking a mixture of liquids of *n*-hexane and carbon tetrachloride, is 1·539 gm/c.c. The density calculated for four molecules per unit cell is 1·520 gm/cm^3. Reflections on the Weissenberg photographs using Cuk$_\alpha$ radiations are *h*01, *h*11 and *h*21. Higher layers were not observed on the rotation or Weissenberg photographs.

Systematic absences were observed for (*hk*0) with $h + k$ odd and 0*k*1 with 1 odd. There were no extra systematic absences for (*hk*1). If in addition to the glide planes indicated by these absences, there are mirror planes perpendicular to *b*-axis. The space group is Pcmn. If mirror planes do not exist, the space group is $Pc2_1n$.

The crystal and physical data of the compound are:

Crystal system		= Orthorhombic
Space group		= Pcmn or $Pc2_1n$
Lattice parameters	a	= 15·418 Å
	b	= 4·897 Å
	c	= 12·334 Å
	α	= $\beta = \gamma = 90°$

Number of molecules per unit cell

	z	= 4
Measured density	dm	= 1·52 gm/c.c.
Calculated density	dc	= 1·53 gm/c.c.
Molecular weight		= 216

Three dimensional intensity data have been collected and the calculation of the structure analysis is in progress.

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ISOPARAMETRIC CURVES AND VEGARD'S LAW PLOTS FOR THE TERNARY SYSTEM Pd–Au–Ag

The palladium-silver-gold alloys, that are made susceptible to precipitation hardening by additions of small amounts of other metals like copper, form the base of a group of dental alloys[1]. A continuous solid solution is found in this ternary system[2]. The melting points of these alloys with varying composition have been studied by Cecil Pauley[3]. The isothermal curves showing the melting points of the alloys indicate that there is a systematic variation in the melting points of the alloys with varying composition. The hardness data of these alloys given by Hafner *et al.*[1] show that the hardness does not vary systematically with composition, but the hardness contours build up a ridge at higher Pd side. In an earlier publication[4], the authors selected a few alloys of the type Pd_λ—$Ag_{(1-\lambda)/2}$ — $Au_{(1-\lambda)/2}$ along the line joining Pd and Ag–Au (50 at %) alloy in the ternary diagram of Pd–Ag–Au with 75, 50 and 25 at % of Pd and studied the variation of the thermal expansion with composition by the X-ray method. It was found that the lattice parameter as well as the coefficient of thermal expansion increased with decrease of palladium concentration, thereby showing a systematic variation with composition unlike the hardness data. It was intended to draw the isoparametric curves for these alloys and see how they vary with composition. For this, the data of the lattice parameters of a number of Pd–Au–Ag alloys have been taken from the literature. Also Vegard's law has been examined for this ternary system in this paper.

The lattice parameters of pure palladium and of the ternary alloys are taken from Kuznetsov's[5] measurements while those of pure silver and gold are taken from Cole's[6] and Stenzel's *et al.*[7] respectively. The position of the alloys with equal lattice parameters (within the limits of experimental errors) are located in the ternary diagram of Pd–Au–Ag system. Fig. 1 shows the isoparametric curves for this system. It can be seen that there is asystematic variation of the

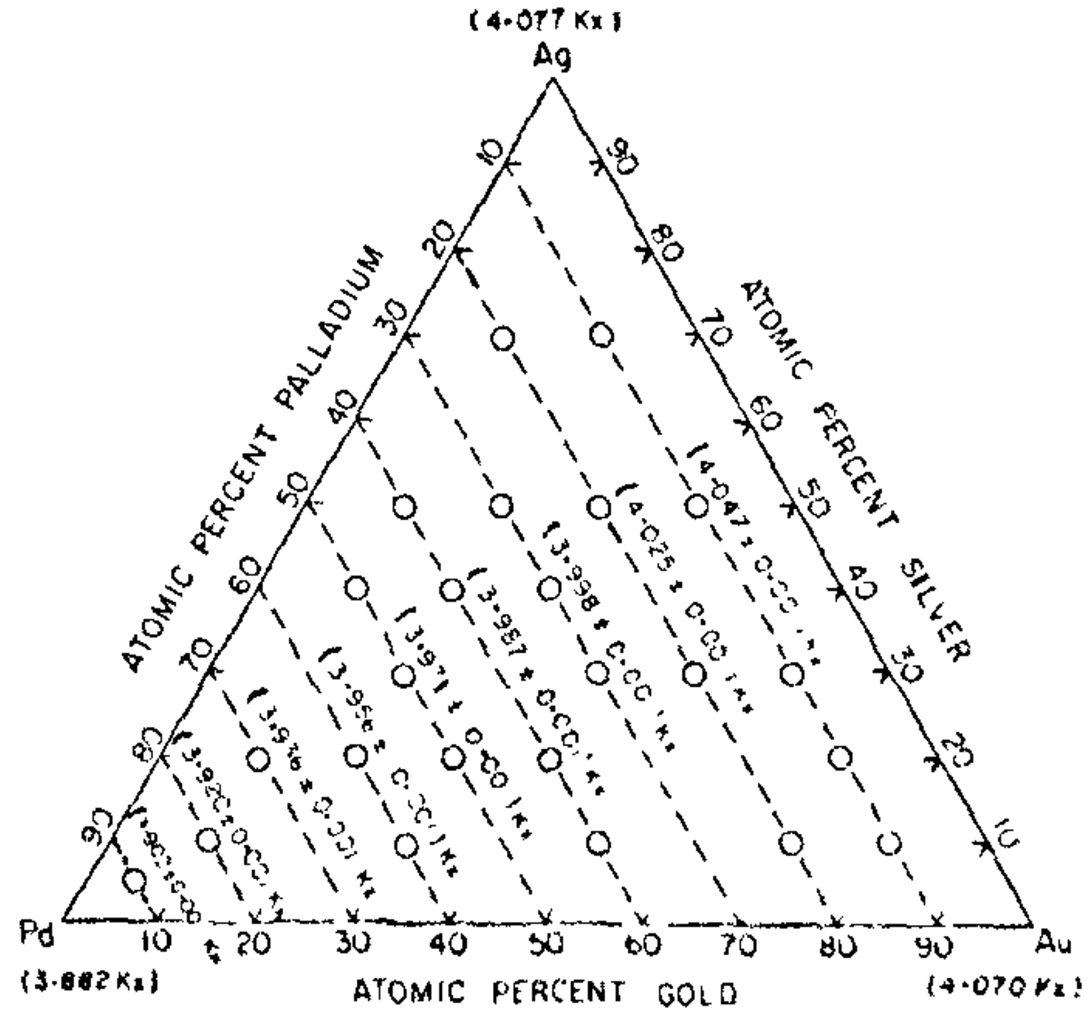

FIG. 1. Isoparametric curves for the ternary system Pd Au Ag.

lattice parameter with composition and it is in good agreement with our earlier results[4].

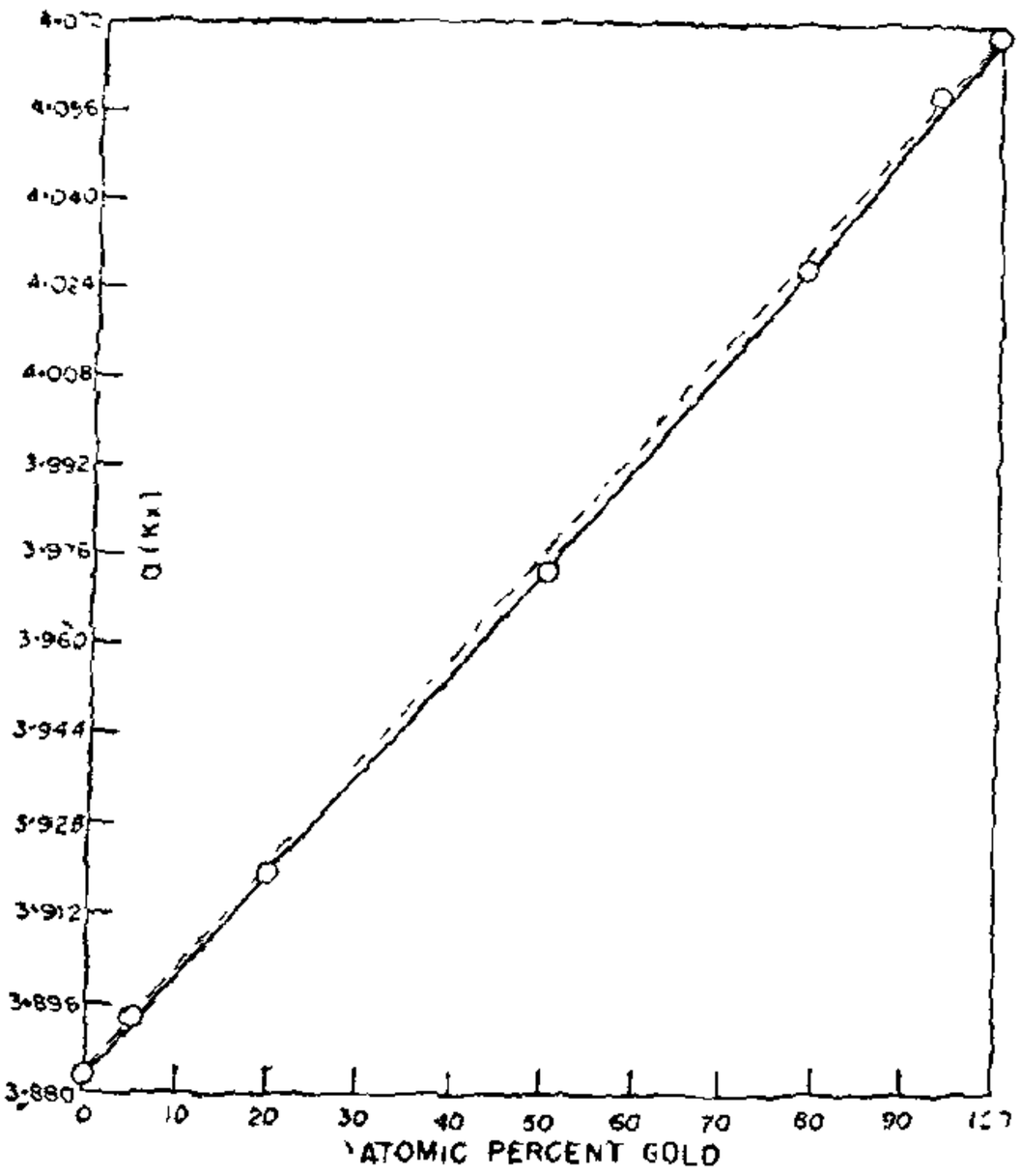

FIG. 2. Vegard's law plot for the binary system Pd–Au.

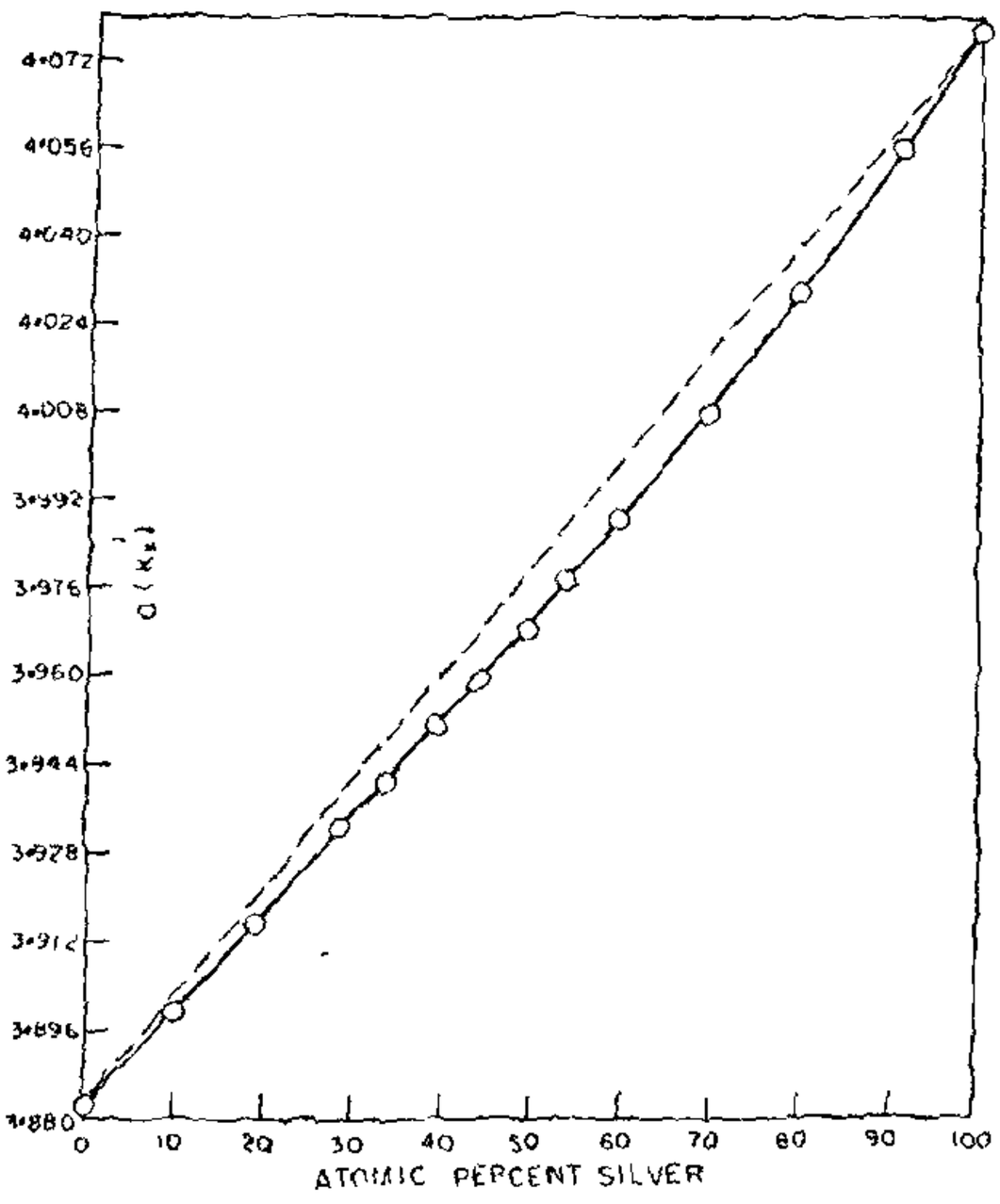

FIG. 3. Vegard's law plot for the binary system Pd–Ag.

Finally, Vegard's law[8] has been examined for this ternary system. The Vegard's law plots for the binary systems Pd–Au[6] and Pd–Ag[7] (Figs. 2 and 3) show a negative deviation in both cases. The Pd–Au–Ag system can be considered as a quasibinary system, with the end components Pd–Au and Pd–Ag, in which the atomic percent of palladium is constant. The Vegard's law plotted on this basis (Fig. 4), using the data from literature[5], also shows a negative deviation as in the case of the binary alloys.

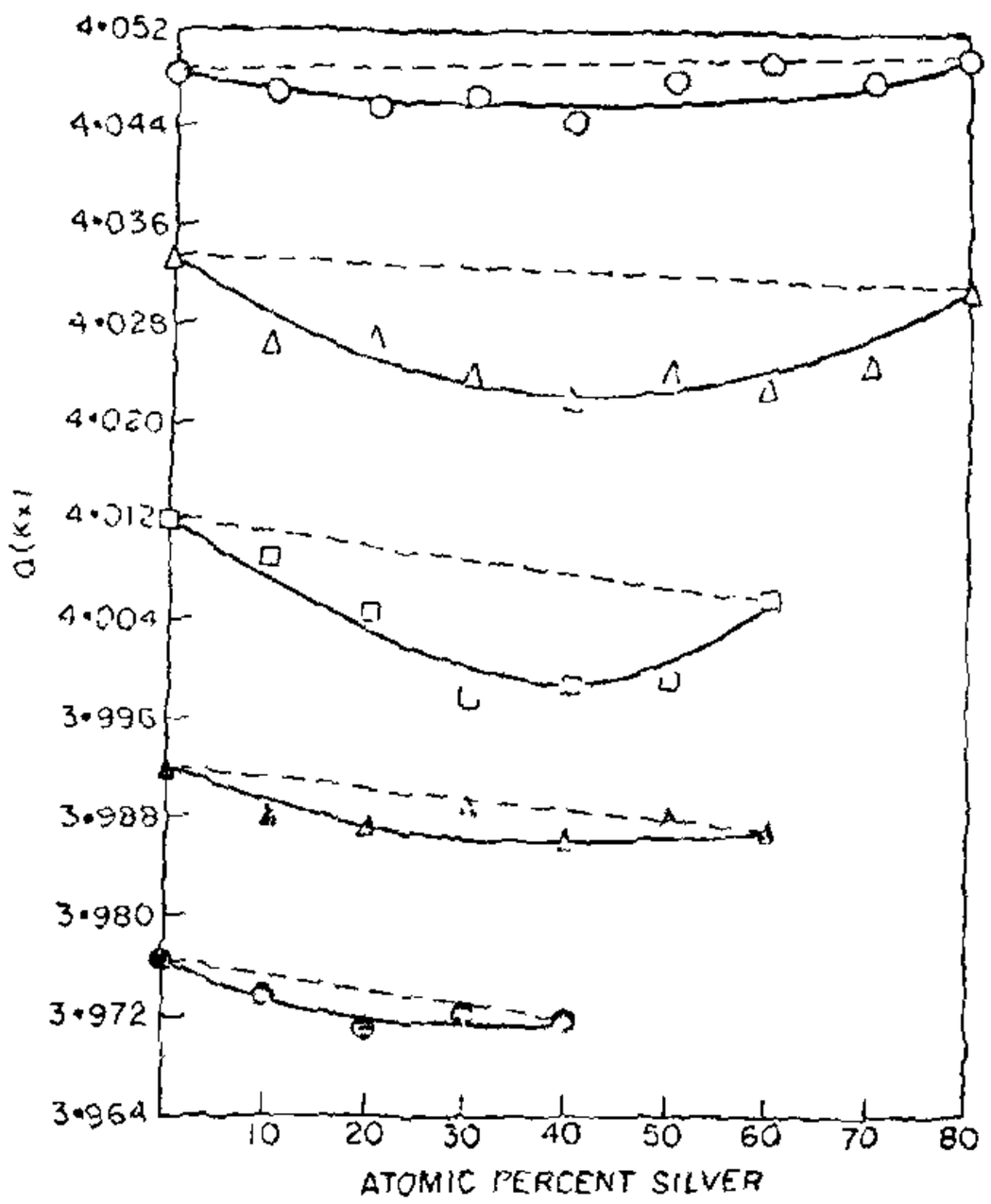

FIG. 4 Vegard's law plots for the ternary system Pd–Au–Ag. (Considering as quasi-binary system Pd–Au and Pd–Ag).

Figure 4 shows a systematic deviation from Vegard's law. It is interesting to note that in the composition range Pd_{20} to Pd_{50}, the deviation decreases with increasing Pd content. As the ionic radius and lattice parameter of palladium are less than those of gold and silver, the increase in Pd content decreases the lattice parameter resulting in negative deviation. A possible explanation of the decrease in the deviation with increasing Pd content is that the size of the ion core of Pd may have changed with its percentage content in the alloy[9].

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THERMAL EXPANSION OF POTASSIUM ACETATE

From m.p. (304° C) to 23° C, potassium acetate is found to have undergone two solid-solid transformations. Initially these were detected by Hazlewood, Rhodes and Ubbelohde[1] as discontinuties in its volume expanison. Hatibarua and Parry[2] investigated the structural basis of the transitions defined as : Form I: Orthorhombic-Trans. temp. 155 °C.—Form II: Monoclininic Trans. temp 75° C—Form III: Monoclinic with superlattice.

The transition I → II is characterised by the change in structural symmetry and termination of the rapid expansion ($\alpha_a \approx 500 \times 10^{-6}$) in the cell constant '*a*' The large thermal expansion may be seen in Fig. 1. The lattice parameters are given in Table I. The structural study revealed that the unit cell of form I consists of ionic double layers of potassium and oxylate ions parallel to (100) firmly bound by ionic forces Between two such double layers are the acetate ions with their methyl ions in contact and bounded by much weaker van der Waal's forces. Anotherpeculiarity is the presence of a void in the unit cell of form I extending through the whole crystal along [100]. The thermal behaviour appears to stem from these two peculiarities. It has been observed that the directions of *b* and *c* axes in from I have remained unchanged through the transition to form II. This means that the orientation of the ionic double layers remains unchanged in the transition. From space group considerations it has been concluded that the acetate ion is no longer constrained to remain parallel to the *a* axis in form II. It moves in the plane (010) with respect to double layers parallel to (100). The progressive decrease of *a* axis from 9·744 Å at 155° C to 9·330 Å at 80° C and the increase in the angle β from 90° to 99·1° in the same range of temperature may be visualised as a shear deformation of the form I along [001] parallel to (100). Thus the structural behaviour is as follows : high temperature form I structure is the statistical average of two positions between which the acetate ions vibrate[3]

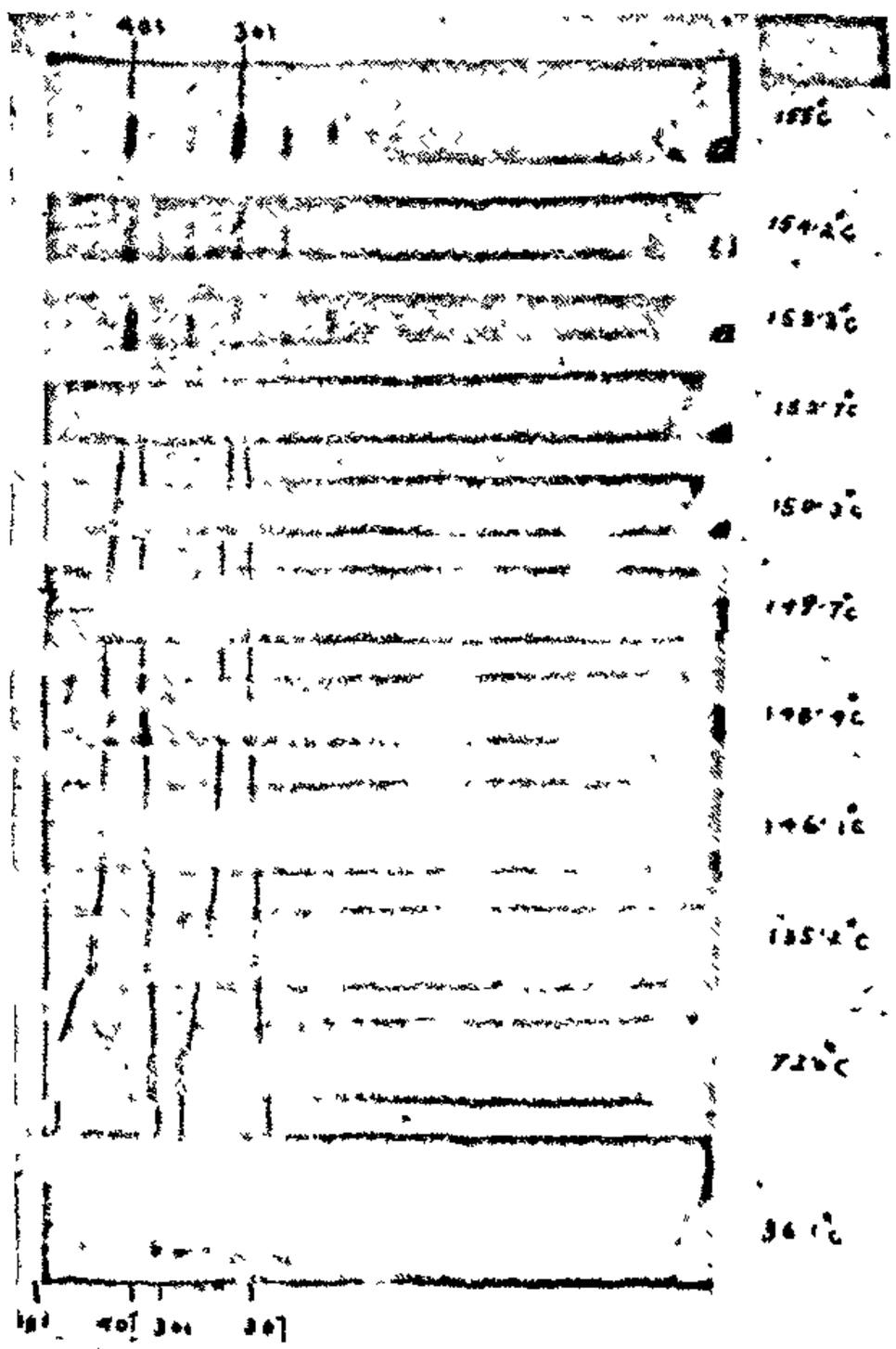

FIG. 1. The movement of pairs of reflexions of the type h01 and h0$\bar{1}$ towards each other with increasing temperature [in between room temperature and (II → I)].

The switching of the acetate ions between the two alternative sites begins at temperatures 3 to 4 degrees below the actual transition temperature. In form II, the *a* axis rapidly contracts and *b* and *c* expand ($\alpha_b \approx -100$, $\alpha_a \approx 40 \times 10^{-6}$) on cooling. As the crystal is cooled from 155° C, the methyl group of the acetate ion in contact with other two in the unit cell begins