positions of the Si and O atoms in crystals of dialkylsilanediols.[17] If the linear (sp) structure were correct, one would expect greatly decreased basicity, since in hydrogen bond formation π-electrons are much less basic than unshared pairs.[18] Pi-bonding involving both electron pairs of oxygen may be important in the nearly linear siloxanes[19] and perhaps also in silanolate ions.

Intermolecular Association of Silanols and Carbinols.—Data on the degree of association also are summarized in Table I. The fraction associated was determined by the deviation from Beer's law with increasing concentration shown by the first overtone of the non-bonded OH absorption.[20]

Only the alkyl substituted silanols and carbinols were sufficiently soluble in CCl_4 to permit measurement of the degree of association. Among these compounds, the silanols are somewhat more associated than the carbinols at any given concentration, but the differences are not large (Table I). The differences between the triethyl and trimethyl compounds in either series are as large as the difference between, *e.g.*, trimethylsilanol and trimethylcarbinol. This suggests that steric factors are very important in determining the degree of association and that decreased hindrance alone might explain the enhanced association of the silanols.

As the concentration of an alcohol in an inert solvent is increased, the first absorption band to appear at lower frequency is by common consent attributed to the O–H vibrations in the hydrogen-bonded dimer, while the broad band appearing at higher concentration and still lower frequency is attributed to higher polymers.[21,22] The silanols, like alcohols, develop two lower-frequency OH bands as the concentration is increased. The position of the first low-frequency band for the compounds studied is given in Table I in the "dimer" column, in terms of the frequency difference ($\Delta\nu$) between this band and the non-bonded OH absorption. There is as yet no firm evidence that the nature of the species responsible for the first low frequency band is the same for alcohols and silanols. However, it is interesting to note that the hydrogen bonds in this first associated species appear to be substantially stronger for silanols than for carbinols. This confirms Batuev's observation that the band shift on polymer formation in trimethylsilanol is exceptionally large.[11] Particularly strong hydrogen bonds in the associated species would be expected for the silanols if they are much more acidic but only slightly less basic than alcohols.

The frequency of the free O–H absorption band of the silanols studied is significantly higher than the free O–H band for alcohols. The silanols absorb in the region 3675–3688 cm.$^{-1}$ while the carbinols absorb at 3600–3614 cm.$^{-1}$. Carbinols generally absorb in the region 3605–3645 cm.$^{-1}$.[23] Batuev and his co-workers previously have noted the high frequency of the free O–H vibration in trimethylsilanol and attributed this shift to enhancement of the O–H bond force constant by the electropositive silicon atom.[11] Pi-bonding from oxygen to silicon, and the probably larger Si–O–H bond angle, may also influence the position of the O–H absorption and at present the evidence seems to us insufficient to explain the phenomenon.

Acknowledgments.—The authors are indebted to Miss Karen J. Lake for her patient assistance with the preparation of diphenylsilanol.

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(17) M. Kakudo and T. Watase, *J. Chem. Phys.*, **21**, 167 (1953); *Bull. Chem. Soc. Japan*, **27**, 605 (1954); M. Kakudo, N. Kasai and T. Watase, *J. Chem. Phys.*, **21**, 1894 (1953).

(18) M. Tamres, This Journal, **74**, 3375 (1952); R. West, *ibid.*, **81**, 1614 (1959).

(19) R. C. Lord, D. W. Robinson and W. C. Schumb, *ibid.*, **78**, 1327 (1956); *cf.* R. F. Curl, Jr., and K. S. Pitzer, *ibid.*, **80**, 2371 (1958).

(20) If the nature of the association reactions were known, our spectral measurements would permit calculations of the equilibrium constants for these reactions.[21] In the absence of definite knowledge about the nature of the association reaction in silanols and carbinols, we have preferred to leave our data in the form of per cent. association at several concentrations. These figures should be directly comparable for silanols and carbinols.

(21) R. Mecke, *Disc. Faraday Soc.*, **9**, 161 (1950); N. D. Coggeshall and E. L. Saier, This Journal, **73**, 5414 (1951); U. Liddel and E. D. Becker, *Spectrochim. Acta*, **10**, 70 (1957).

(22) F. A. Smith and G. C. Creitz, *J. Research Natl. Bur. Standards*, **46**, 151 (1951).

(23) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd Ed., Methoen and Co., London, 1958, p. 97.

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[Contribution from the Chemistry Department of St. Louis University]

Reactions between Dry Inorganic Salts. X. The Effect of Rubidium Chloride on the Transition Temperature of Cesium Chloride

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A study of the effect of rubidium chloride on the transition temperature of cesium chloride has been made by means of the high temperature X-ray camera. It has been established that increasing amounts of added rubidium chloride cause a spectacular lowering of the transition temperature and that, at room temperature, up to 30 mole % of the high temperature form of cesium chloride may remain in the rubidium chloride in the form of a solid solution.

In a previous publication[2] it was shown that addition of cesium bromide to cesium chloride raises markedly the temperature at which the Pm3m→Fm3m transition begins and that the

(1) Taken in part from theses presented to the faculty of St. Louis University for the degree of Master of Science.

(2) L. J. Wood, Wm. Secunda and C. H. McBride, This Journal, **80**, 307 (1958).

resulting Fm3m phase consists of a solid solution of Fm3m cesium chloride and a previously unknown Fm3m form of cesium bromide.

In this work study has been made of the changes in the Pm3m→Fm3m temperature caused by increasing amounts of rubidium chloride added to cesium chloride. In 1910 Zemczuzny and Rambach[3] reported breaks in cooling curves for mixtures of cesium chloride with small amounts of rubidium chloride which can now be correlated with the Fm3m→Pm3m transition. With increasing amounts of rubidium chloride, these breaks in the cooling curves became smaller and occurred at lower temperatures up to about 10% rubidium chloride after which they could no longer be observed. The results presented below, obtained by means of the X-ray camera, will show that the transition temperature lowering does not stop at 10% rubidium chloride and that the Fm3m phase that is stable at room temperature consists of a solid solution of Fm3m (high temperature form) cesium chloride in rubidium chloride.

Bridgman[4] has shown that at sufficiently high pressures rubidium chloride undergoes a discontinuity in its density curve at room temperature, and Pauling[5] has shown that this discontinuity may correspond to a transition from Fm3m symmetry to Pm3m symmetry. Jacobs[6] confirmed the discontinuity in the density curve of rubidium chloride, reported by Bridgman, but using X-ray analysis at high pressures failed to find any Pm3m diffraction lines. However, Wagner and Lippert[7] have shown that rubidium chloride can exhibit Pm3m symmetry when sublimed onto Pm3m thallous chloride at −190°. It therefore appears possible that if rubidium chloride can, in fact, exist in the Pm3m form at low temperatures, it might form a solid solution with Pm3m cesium chloride. Such a solid solution might be expected to undergo the Pm3m→Fm3m transition at a higher temperature than that of pure rubidium chloride. It has been part of the purpose of this investigation to examine this possibility.

Apparatus and Materials

The cesium chloride and the rubidium chloride were the same as previously described.[2,21] All salt mixtures, unless otherwise indicated, were prepared by thoroughly mixing powered samples of the previously melted pure salts. Each mixture was then fused, cooled to room temperature, ground and stored in a desiccator until needed. The salt mixtures were examined at high temperatures by means of a furnace built into the powder camera furnished by the General Electric Company for use with the XRD-3D X-ray diffraction unit.[8] The sample tube, which had very thin walls and an outside diameter of 0.3 to 0.4 mm. was mounted on a ceramic shaft in such a way that it could be rotated at the center of the camera. The molybdenum Kα doublet was used for all the diffraction analyses.

A control thermocouple for automatically controlling the temperature was placed above the sample tube and just outside the X-ray beam. This thermocouple was connected to a thyratron shift-phase control circuit.[8] A temperature measuring thermocouple was placed below and just outside the X-ray beam. This thermocouple was connected to a type K Leeds and Northrup potentiometer. This thermocouple was calibrated by observing its reading when a sample of pure cesium chloride was at its transition temperature of 472° as recently found by Wood and co-workers.[2] The transition temperature was approached from the low temperature side, and great care was taken to avoid overshooting the observation temperature.[9] X-Ray patterns were photographed at temperatures just above, just below and very near to the Pm3m ⇄ Fm3m transition temperature. The sample was exposed to X-rays for 9 hr., and the temperature was checked at 15 min. intervals for the entire time. By adjusting the automatic temperature control when necessary, the over-all temperature variation was held to about one degree centigrade. This same exacting procedure was followed, when necessary, for all observations reported below. Efforts to calibrate the temperature measuring thermocouple by comparison with a supplementary thermocouple placed at the same position were not successful. The reasons for this failure are important but cannot be discussed here.

Results and Discussion

The unit cell edge of Fm3m cesium chloride was determined at 475 and 480° (Table I) by comparison with the unit cell edge of aluminum and with that of Pm3m cesium chloride.[10] The unit cell edge of aluminum was obtained at higher temperatures by the use of a temperature coefficient of expansion determined by Hidnert and Krider (2.57×10^{-5}).[11] Several unit cell edge values for Fm3m cesium chloride and for rubidium chloride have been calculated for several temperatures that will be involved in the discussion that follows (Table II). Because of too few data, neither the 4.2×10^{-4} coefficient of Wagner and Lippert for Fm3m cesium chloride nor the 2.7×10^{-4} coefficient for rubidium chloride can be said to be rigorously established, but both may be considered adequate for the present use. Both of these coefficients seem reasonable when compared with the very carefully determined temperature coefficient of expansion of 2.18×10^{-4} for potassium chloride as reported by Glover.[12] The relation between these coefficients becomes Fm3m CsCl: Fm3m RbCl:Fm3m KCl = 4.2×10^{-4}: 2.7×10^{-4}: 2.18×10^{-4}.

Using the high temperature X-ray camera and the thermocouples described above, a study was made of the Pm3m→Fm3m transition in mixtures of rubidium chloride and cesium chloride containing increasing percentages of rubidium chloride (Table III). At sufficiently elevated temperatures (always lower than the transition temperature of pure cesium chloride) these mixtures consisted of a single crystalline phase having Fm3m symmetry. The unit cell edge of this phase was always larger than that of rubidium chloride and smaller than that of Fm3m cesium chloride (calculated) at the

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(3) S. F. Zemczuzny and F. Rambach, *Z. anorg. Chem.*, **65**, 418 (1909).

(4) P. W. Bridgman, *Phys. Rev.*, **57**, 237 (1940).

(5) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1945.

(6) R. B. Jacobs, *Phys. Rev.*, **54**, 325 (1938).

(7) G. Wagner and L. Lippert, *Z. physik. Chem.*, **B33**, 297 (1936).

(8) C. M. McBride, M.S. Thesis, St. Louis University, 1957.

(9) This was necessary, because of the hysteresis found by Wood and co-workers. Upon cooling from a few degrees above 472° the Fm3m ⇄ Pm3m transition occurs at 465°. Preliminary results obtained in the author's laboratory indicate that if the 472 degree transition is exceeded only slightly and if the cesium chloride remains at this high temperature for only a short time, the transition range is narrowed. It appears possible that untransformed nuclei may, under these circumstances, remain for a brief time. Such nuclei could seed the transition back to the low temperature form as the temperature is lowered. These observations, which are not yet conclusive, are to be reported in a future communication.

(10) L. J. Wood and J. Wm. Vogt, THIS JOURNAL, **66**, 1259 (1944).

(11) Peter Hidnert and H. S. Krider, *J. Research Natl. Bur. Standards*, **48** (1952).

(12) R. E. Glover, *Z. Physik*, **138**, 222 (1954).

TABLE I

SOME UNIT CELL EDGES FOR F_m3_m CESIUM CHLORIDE AND FOR RUBIDIUM CHLORIDE

	a_0 (Å.)	Reported temp. (°C.)	Observer	Remarks
	7.046	475	This work	Aluminum used as an internal standard
Fm3m CsCl	7.043	475	This work	Compared with a_0 = 4.123 Å.[16] for Pm3m CsCl at 30°
At or near Pm3m → Fm3m transition temp. (472°)	7.042	482	Menary, Ubbelohde, Woodward[13]	Based on one line from a single crystal determination
	7.04	445[a]	Wagner and Lippert[14]	Originally reported as 7.02 kX. units. Recalcd. by comparison with a_0 = 4.123 Å. for Pm3m CsCl at 30°
	7.05	475		Calcd. by the use of the Pm3m:Fm3m cell edge ratio = 0.6[b]
Fm3m CsCl	7.11	480	This work	Compared indirectly with aluminum as an internal standard
At slightly above the Pm3m → Fm3m transition temp. (472°)	7.10	480	This work	Compared with a_0 = 4.123 Å.[10] for Pm3m CsCl at 30°
	7.10	460[c]	Wagner and Lippert[14]	Originally reported as 7.07 kX. units. Recalcd. by comparison with a_0 = 4.123 Å. for Pm3m CsCl at 30°
	6.591	30	Wood and Paproth[21]	Aluminum used as an internal standard
Fm3m RbCl	6.645	260	This work	Aluminum used as an internal standard
	6.658	259	This work	Compared with a_0 = 6.591 for RbCl at 30°
	3.74	−190	Wagner and Lippert[7]	RbCl deposited on Pm3m TlCl at −190°
Pm3m RbCl	3.82	30		Extrapolated from −190° to 30°[d]
	3.95	30		Calcd. by the use of the Pm3m:Fm3m cell edge ratio = 0.6[2]

[a] Work in progress in the author's laboratory by G. A. McLaren on the cesium chloride–potassium chloride system has shown that as little as one mole % of potassium chloride present in cesium chloride as impurity could be expected to lower the transition by 10 to 15°. This small amount of potassium chloride would lower the unit cell only a few units in the third decimal place and easily could go undetected. [b] An extrapolated value of 4.23 Å. was first obtained for 475° by the use of what appears to be an accurately determined temperature coefficient by Menary, Ubbelohde and Woodward[13] which was then divided by the Pm3m:Fm3m cell edge ratio.[2] This calculation cannot be expected to yield more than approximate results. [c] This temperature is 15 degrees above the transition temperature reported by Wagner and Lippert. The results reported in this work confirm the rather sudden large increase in unit cell edge immediately above the transition temperature reported by Wagner and Lippert. Precision measurements of the temperature coefficient of expansion of F_m3_m cesium chloride in the first few degrees above the transition temperature might make a very interesting study. [d] A temperature coefficient of 3.8×10^{-4} was used for this calculation which was based on the TlCl unit cell edge value of Wagner and Lippert at −190° and at room temperature. The 3.82 value must be considered to be only an approximation.

TABLE II

UNIT CELL EDGES AT VARIOUS TEMPERATURES AS CALCULATED BY MEANS OF THE LINEAR COEFFICIENT OF EXPANSION AND AN OBSERVED CUBE EDGE AT SOME KNOWN TEMPERATURE

Fm3m CsCl $a_t = 7.10 + 4.2 \times 10^{-4} (t - 480)$ (Wagner and Lippert[13]) T, °C.	 a_0 (Å.)	Fm3m RbCl $a_t = 6.652 + 2.7 \times 10^{-4} (t - 260)$ (This work) T, °C.	 a_0 (Å.)
525	7.119[a]		
480 obsd.	7.10		
365	7.052	365	6.680
260	7.008	260	6.652 obsd.
30	6.911	30	6.591 obsd.

[a] The previously reported relative value of 7.075 Å.[2] was not calibrated by means of an internal standard and was not corrected for opacity of the sample. This value, on an absolute basis, is somewhat too low.

TABLE III

COMPLETION TEMPERATURES FOR THE CESIUM CHLORIDE Pm3m → Fm3m TRANSITION IN CESIUM CHLORIDE–RUBIDIUM CHLORIDE MIXTURES[a]

Mole % RbCl	Max. temp. for Pm3m + Fm3m °C.	Min. temp. for pure Fm3m, °C.	Completion temp. for Pm3m → Fm3m °C.
0			472
5	434	444	438
10	390	400	395
20	350	360	355
50	210	220	215

[a] Many more tests were made both above and below the completion temperatures. This summary includes only those tests that were immediately above (column 3) and immediately below (column 2) the completion temperature of the cesium chloride Pm3m → Fm3m transition.

corresponding temperature (Table II), and this unit cell edge decreased for larger additions of rubidium chloride. In view of these observations it seemed reasonable, indeed necessary, to conclude that in the region of the single crystalline phase, all of the cesium chloride existed in the Fm3m form in solid solution with the rubidium chloride.

This conclusion is in complete agreement with freezing point data shown in Fig. 1.[15] The beginning and the end of freezing were observed in a thermally insulated, all-glass apparatus which was heated electrically. The thermocouple was calibrated by means of the freezing point of pure cesium chloride, as determined by comparison with the freezing point of U. S. Bureau of Standards aluminum and pure potassium chloride.[16] The

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(13) J. W. Menary, A. R. Ubbelohde and I. Woodward, *Proc. Roy. Soc. (London)*, **A208**, 158 (1951).

(14) G. Wagner and L. Lippert, *Z. physik. Chem.*, **B31**, 263 (1936).

(15) G. J. Riconalla, M.S. Thesis, St. Louis University, 1959.

(16) Thomas J. Flautt, Jr., B.S. Thesis, St. Louis University, 1953.

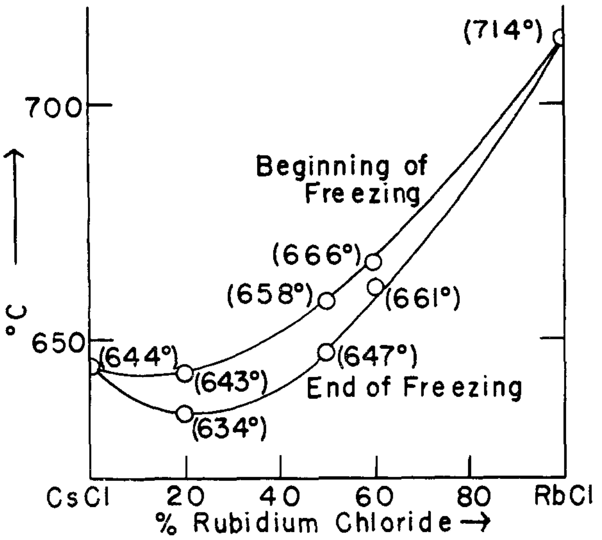

Fig. 1.—Melting point diagram for the CsCl–RbCl system.

freezing point of pure rubidium chloride used in Fig. 1 is due to Richards and Meldrum.[17]

At lower temperatures the X-ray lines showed both an Fm3m pattern and a Pm3m pattern, but as the temperature was raised, the intensities of the Pm3m lines decreased and finally disappeared as the low temperature form of cesium chloride went completely into the Fm3m solid solution. This disappearance temperature, which was fixed by the percentage of rubidium chloride, was determined by means of the high temperature X-ray furnace. Beginning at a temperature in the two phase region, each sample was carefully heated to the observation temperature and held at this temperature for from 30 minutes to 2 hours, before applying the X-rays. X-Ray patterns were made for each mixture at successive 10 degree increments. When the X-ray lines for the Pm3m pattern barely could be observed at one temperature and could not be observed at a temperature 10 degrees higher, the disappearance temperature of the Pm3m phase was taken to be half way between the two temperatures (column four, Table III). Considering the likely situation that residual disappearing crystals (or crystals of a new phase just forming) may not be detected by the X-rays over a small temperature range and also considering the limitations inherent in the actual measurement of the temperature described above, it appears probable that the accuracy in observation of the temperature at the phase change boundary was about plus or minus five degrees.

Two questions are now to be answered. First, is the Pm3m pattern that appears upon cooling due to pure cesium chloride separating out of the Fm3m solid solution, or is this pattern due to a solid solution of low temperature cesium chloride and some Pm3m rubidium chloride; and secondly, does the Fm3m phase eventually become pure rubidium chloride due to the complete unmixing of the Fm3m solid solution?

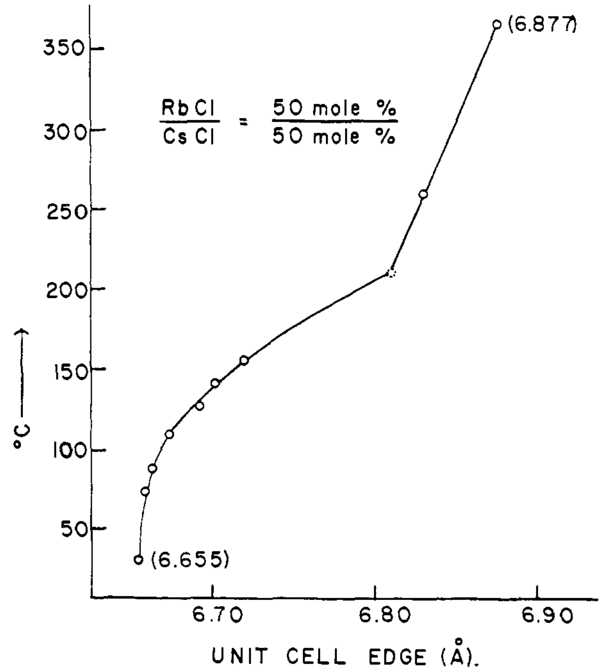

Fig. 2.—Temperature *vs.* unit cell edge for the 50:50 mole % CsCl–RbCl mixture.

To answer these questions a careful X-ray analysis was made of the 50% molar mixture over a temperature range from 365° to room temperature (Fig. 2). The room temperature X-ray results for the previously melted and thoroughly annealed sample (Table IV) showed clearly a fairly satisfactory Fm3m pattern in the presence of a very dense Pm3m pattern.[18] A direct comparison of the lines on this film with the lines of a 50% molar mechanical mixture of pure rubidium chloride and cesium chloride showed no detectable difference in the displacements of the Pm3m lines from the zero position in the two cases, which indicated that the Pm3m phase that separated out from the Fm3m solid solution upon cooling was pure low temperature cesium chloride. However, the lowering of the unit cell edge of cesium chloride by Pm3m rubidium chloride would not be great (Table II) and the effect of small amounts, up to several per cent., of rubidium chloride might not be detected by X-ray analysis. The purity of this Pm3m phase was tested further by the more sensitive index of refraction technique.[19] After heating a mechanical mixture of cesium chloride and rubidium chloride powders for three weeks at 175°,[15] there was a definite increase in the index of the rubidium chloride[20] which undoubtedly was due to the presence of some transformed Fm3m cesium chloride in the rubidium chloride lattice. On the other hand, there was no lowering in the index of refraction of the residual Pm3m cesium chloride which must be taken as a compelling indication that no transformed Pm3m rubidium chloride has entered the cesium chloride lattice under these conditions. This conclusion is in

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[17] T. W. Richards and W. B. Meldrum, THIS JOURNAL, **39**, 1819 (1917).

[18] For lower percentages of rubidium chloride, the relative number of moles of the Fm3m phase was less, and it became difficult to detect the X-ray lines of this pattern in the presence of the dense Pm3m phase.

[19] L. J. Wood and A. J. Frank, *Anal. Chem.*, **23**, 695 (1951).

[20] L. J. Wood and L. J. Breithaupt, Jr., THIS JOURNAL, **74**, 2355 (1952).

TABLE IV

ROOM TEMPERATURE X-RAY ANALYSIS OF A PREVIOUSLY MELTED 50 MOLE % CsCl–RbCl MIXTURE (FILM SM-10)

d_{hkl}, Å., Obsd.	Pm3m *hkl*	d_{hkl}, Å., calcd. ($a_0 = 4.123$)	Fm3m *hkl*	d_{hkl}, Å., calcd. ($a_0 = 6.655$)
4.143	100	4.123		
3.891			111	3.842
3.362			200	3.328
2.929	110	2.915		
2.373	111	2.380		
2.061	200	2.062		
2.017			311	2.007
1.922			222	1.921
1.846	210	1.844		
1.681	211	1.683		
1.488			420	1.488
1.459	220	1.458		
1.358			422	1.358
1.301	310	1.304		
1.191	222	1.190		
1.100	321	1.102		

agreement with observations by Wagner and Lippert[7] who found that Pm3m rubidium chloride deposited on thallous chloride at −190° changed back to the Fm3m form when warmed to room temperature.

Beginning at 365°, the 50:50 mixture produced only an Fm3m phase at temperatures down to 215° (Fig. 2). At 365° the unit cell edge of the Fm3m phase was 6.877 Å. which was more than 6.680 Å. calculated for the cell edge of rubidium chloride at this temperature (Table II) but less than 7.052 Å. calculated by extrapolation for Fm3m cesium chloride and not far from 6.866 Å., the midpoint between these two values: this, in spite of the fact that the temperature is more than 100 degrees below the transition point of pure cesium chloride (472°).

Below 215° the temperature rate of decrease of the unit cell edge of the Fm3m phase suddenly becomes much larger due to the loss of cesium chloride as Pm3m cesium chloride forms in increasingly larger amounts. Beginning at about 130° the curve changes gradually until the decrease in unit cell edge becomes little more than might be expected to result from cooling the Fm3m phase. However, the results of Table IV show clearly that the unmixing of the Fm3m solid solution is far from complete at room temperature. This is so because the unit cell edge value of 6.655 Å. for the Fm3m phase is larger than 6.591 Å., the cell edge value for pure rubidium chloride,[21] and smaller than 6.911 Å., the room temperature extrapolated value for Fm3m cesium chloride. It was at first thought possible that a new phase begins to appear somewhere in the temperature interval 130 to 100°, but no new X-ray lines could be found. It is now believed that unmixing of the solid solution continues through this range of temperature and continues on down to room temperature. This view was confirmed by preliminary tests at 0 and −20°, which indicated further unmixing at these lower temperatures.

The composition of the Fm3m solution of Table IV was determined by testing a new series of mixtures containing increasing amounts of rubidium chloride (Table V). As the percentage of rubidium chloride increased from 50%, the intensity of the Pm3m pattern decreased progressively, until at 70 mole % of rubidium chloride the Pm3m pattern could no longer be observed even after thorough annealing. When as little as 1% of pure cesium chloride was mixed mechanically with this 70% sample, the Pm3m pattern again could be seen easily. The observations show that the solubility of cesium chloride in rubidium chloride at room temperature cannot be far from 30 mole % and that the resulting solid solution has Fm3m symmetry.

TABLE V

ROOM TEMPERATURE X-RAY ANALYSIS OF MIXTURES CONTAINING 50–70 MOLE % RbCl

Composition of mixt. in mole % CsCl	RbCl	Description of Pm3m[a] cesium chloride pattern
50	50	Strong and definite
35	65	Definite
$33^1/_3$	$66^2/_3$	Weak but definite
$31^2/_3$	$68^1/_3$	Weak—only one Pm3m line
30	70	No Pm3m lines obsd.

[a] Each mixture produced a strong Fm3m pattern.

If Vegard's law be assumed, the composition of this solid solution and the unit cell edge value of 6.655 Å. shown in Table IV can be used for calculating a hypothetical room temperature unit cell edge for Fm3m cesium chloride. The value obtained is 6.803 Å. which is appreciably less than the extrapolated value of 6.911 Å. shown in Table II. The agreement is as good as could be expected, considering the uncertainty of the extrapolation and the possibility that Vegard's law may not hold rigorously.

A series of observations was made on an 85:15 molar mixture of rubidium chloride and cesium chloride over a wide range of temperature. At all temperatures only an Fm3m solid solution was found having about the unit cell edge and temperature coefficient of expansion to be expected for such a mixture.

In view of the various observations described above, it does not seem unreasonable to postulate the possibility of an Fm3m→Pm3m rubidium chloride transition in the presence of Pm3m cesium chloride at lower temperatures, although no such transition was observed at temperatures included in this investigation. It is hoped that quantitative measurements made in the low temperature range can be reported at some future time.

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(21) L. J. Wood and H. H. Paproth, *Anal. Chem.*, **28**, 1427 (1956).