Significance and Importance of Thermal Expansion:

[*]Mohammed Wahed Hussain, Mohammed Yousuf Hussain Ansari

Department of Physics Chaitanya Postgraduate College Warangal (T S)
Department of Physics Government Degree College Warangal (T S)
Corresponding Author: Mohammed Wahed Hussain

Abstract: *Basic and foremost objective of Solid-state Physics is to explore lattice dynamics. It can be accomplished only after obtaining comprehensive knowledge of Lattice properties such as specific heat, elastic constants, and thermal expansion coefficients. Specific heat and elastic constants have been measured for a large number of elements in pure form as well as in the form of important binary alloys, over a wide range of temperatures, from the neighborhood of absolute zero to the temperatures beyond melting points. According to Debye characteristic temperature (0D), the low temperature limit must be in the vicinity of 0o/100, where the wavelengths of the thermal waves are longer than inter atomic distance and the solid is regarded as elastic continuum.Though data on specific heat and elastic constants have been obtained at various temperatures, complementary data on thermal expansion, can only tell us about the an-harmonic nature of the interatomic forces. In metals the free electrons also contribute to the heat capacity, in the same way it also contributes to the expansion of solid. Theoretically we might expect the electronic contribution to the expansion coefficient changes linearly with temperature. At high temperature vibration of atoms is anharmonic so the expansion takes place in the crystal. Whenever vibration of atom is harmonic, there will be no expansion. It is very important and related to several physical properties such as melting points, compressibility etc.*

Keywords; *Lattice constant, Thermal Expansion, Gruneisen parameter*

I. Introduction

The thermal expansion of solids is a basic physical property representing the dimensional changes in a solid induced by a change in temperature. It is of technical importance as it determines the thermal stability of a crystal. The thermal shock resistance of crystals depends on the thermal expansion (Campbell, 1962). The thermal expansion characteristics decide the choice of material for construction of metrological instruments. In modern epitaxial device technology, lattice mismatch is an important factor; this is related to the thermal expansion behavior. (Kommichau et al., 1986). In nuclear fuel technology, the thermal expansion is a deciding factor in the choice of container material (Fullam, 1972).

The thermal expansion coefficient (α) is related to several other physical properties of crystal. Thus, it is related to the melting point (Tm), the product α Tm being approximately constant for a family of crystals (Van Uitert et al., 1977). Hanneman and Gatos (1965) proposed that the coefficient of expansion α is simply related to the compressibility; Sirdeshmukh (1967) modified this relation. Askill (1965) showed that the self-diffusion coefficients of metals correlate with their expansion coefficients. Sirdeshmukh (1966) showed that the thermal expansion of alkali halides is closely related to the effective ionic charge. Houska ad Stein (1966) discussed the relationship between the thermal expansion and the atomic vibration amplitudes. Khan (1974) observed a relation between the coefficient of expansion of alkali halides and the ionic radius ratio.

The knowledge of thermal expansion is necessary in the experimental determination of the temperature variation of elastic constants, refractive index, dielectric constants and photo elastic constants. The thermal expansion data are also needed in the conversion of C_p into C_v.

The potential energy curve of a solid is asymmetric. This makes the thermal vibrations enharmonic. Thermal expansion of a solid owes its origin to this anharmonicity. Through a simple calculation for linear lattice, Kittel (1971) expresses the thermal expansion in terms of the anharmonicity parameters. In a more elaborate way, it can be shown that the thermal expansion is related to the lattice dynamics of the crystal. Each mode of vibration γ_i has its corresponding Gruneisen parameter γ_i and also makes its contribution C_i to the specific heat. The thermal expansion coefficient α is given by

$$\alpha = (1/3 \ BV) \ i\text{€} \ \gamma i \ Ci$$

where β is the bulk modules. Thus, the comparison of α calculated from the lattice vibration spectrum with the experimental values provides a good check on the lattice dynamical model (Vetelino et al., a, b, 1970).

Review of studies on thermal expansion:

There has been a considerable amount of work on thermal expansion of solids. This work is scattered in literature. A review of thermal expansion can be found in Krishnan (1958) and Krishnan et al., (1977). Krishnan et al., also included a very good bibliography on thermal expansion. Yates (1972) reviewed the work on alkali halides and alkaline earth fluorides.

Some of the recent work on thermal expansion is reviewed here. The work reviewed hereby mostly pertains to the recent work done during the last two decades. The review is by no means exhaustive but refers only to such contributions which cover a large number of crystals or those which involve some new feature.

Bailey and Yates (1967) determined the thermal expansion of crystals with CsC1 structure at low temperatures. Pathak and Vasavada (1992) and Pathak et al., (1973) reported the thermal expansion of four alkali halides at thigh temperatures by the x-ray method. Rapp and Merchant (1973) and Srivastava and Merchant (1973) determined the thermal expansion of fifteen alkali halides and studied the temperature variation of Gruneisen constant. Hovi and Pirinen (1972) determined the thermal expansion of rubidium halides at low temperatures by the x-ray method. White (1965) and White and Collins (1972) determined the thermal expansion of fourteen alkali halides at very low temperatures and calculated the Gruneisen constant as a function of temperature. Yagi (1978) was first to determine the pressure variation of thermal expansion of some alkali halides using a special camera. Boehler and Kennedy (1980) made measurements of LiF using a compression method and obtained results similar to Yagi's.

The thermal expansion of crystals with the rutile structure has received some attention. Krishna Rao and coworders (1967, 1967, 1970, 1973) reported the thermal expansion of VO_2, IrO_2, TiO_2 and GeO_2 by the x-ray method. Kirby (1967) measured the thermal expansion of TiO_2; an interpretation of this results was given by Shaner (1973) in terms of Gruneisen's theory.

The thermal expansion of a number of crystals with schelite structure was determined by Deshpande and Suryanarayana (1969, 1972) and Bayer (1972). A discussion of given by Suryanarayana and Deshpande (1978) in terms of changes in anharmonicity and changes in the orientation of the BO_4 groups. The thermal expansion of a large number of crystals belonging of four structure types was reviewed by Krishna Rao and Deshpande (1978). The structures are scheelite, ADP, rutile and calcite. The anisotropy in thermal expansion in these crystals is co related with structural features.

The thermal expansion of CdS and ZnS in the wurtzite phase was determined by Reeber and Kulp (1975) and Reeber and Powell (1967) by the x-ray method. Roberts et al., (1981) determined the thermal expansion of ZnS in the sphalertie phase. The thermal expansion of a number of diamond like crystals was determined by Slack and Bartran (1975).

The A_{15} structure compounds have become important because of their superconducting properties. The thermal expansion of V_3Ge and V_3Si at low temperatures was reported by Testardi (1972). Rao and Sirdeshmukh (1980) reported the thermal expansion of V_3Si at elevated temperatures. Herold et al., (1981) and Somi Reddy and Suryanarayana (1983; 1984) have measured the thermal expansion of a number of crystals with the A_{15} structure.

The chalcopyrite structure crystals have semiconducting properties. Kishtaiah et al., (1981, a, b, c) have reported the thermal expansion of three crystals with this structure.

They observed an anomaly in the case of silver indium selenide. Dues et al., (1983) and Neuman et al., (1984) determined the thermal expansion of copper indium selenide and copper indium telluride at low temperatures. Neumann (1983) calculated the Gruneisen constants of some chalcopyrite type crystals from their elastic constants.

The thermals expansion of a number of garnets was measured over a wide temperature range by Geller et al., (1969). Reddy and Reddy (1973) measured the thermal expansion of some ferrites. An interesting contribution was made by Krause et al., (1983) who measuring the thermal expansion of some organic conductor crystals. Using the thermal expansion data they calculated the Debye temperatures of these crystals.

The theories of thermal expansion have been reviewed by Anderson (1967). Apart from the basic theory of Gruneisen, Anderson discusses negative thermal expansion, the acoustic Gruneisen parameters and the effect of pressure of thermal expansion. An atomistic expression for thermal expansion of elemental solids was given by Plendl (1973). The physics of Gruneisen parameter was critically examined by Harris and Avrami (1972). The calculation of Gruneisen constant from potential functions has been carried out by Kachhava and Saxena (1965), Sirdeshmukh and Rao (1972, 1975) and Pandey and Pandey (1980). The various methods of calculating Grunenisen parameters from elastic data were reviewed by Knopoff and Shapiro (1969).

Review of physical properties of fluorite type crystals:

Fluorite (CaF_2) has a cubic structure with space group Fm3m and four molecules per unit cell. Several fluorides, halides and oxides have this structure. The fluorides and oxides are very stable, insoluble in water and have high melting points. Some of these crystals have proved to be of practical importance. CaF_2, SrF_2 and

BaF_2 have useful transmission characteristic in the infrared region. Recently they have been used as epitaxial dielectric films in this film devices. CdF_2 becomes a semiconductor with suitable doping. PbF_2 and $SrCl_2$ have prominent superionic conducting properties. UO_2 and ThO_2 are useful in nuclear technology. Because of their simple structure and simple interatomic bonding, it is possible to use these crystals for testing solid state theories. Consequently, considerable amount of work, both theoretical and experimental, has been done on these crystals. A number of aspects have been discussed by Hayes (1977) in his book.

The elastic constants of CaF_2, SrF_2 and BaF_2 were reported by Haussuhl (1963). BaF_2 is one of the very few crystals having elastic isotropy. The temperature variation of elastic constants at low temperatures has been studied for CaF_2 by Haufmann and Norwood (1960), for BaF_2 by Gerlich (1964a), for SrF_2 by Gerlich (1964b) and for CdF_2 by Alterovitz and Gerlich (1970). The elastic constants of PbF_2 and BaF_2 have been measuring over a wide temperature range (Manasreh and Pederson 1984, 1985). The pressure variation of elastic constants was carried out for CaF_2 by Wong and Schuele (1967), for SrF_2 by Alterovitz and Gerlich (1970a) for BaF_2 by Gerlich (1968) and for CdF_2 by Alterovitz and Gerlich (1970b). the pressure variation of elastic constant of PbF_2 was determined by Riai and Sladek (1980). The third order elastic constants of CaF_2, SrF_2 and BaF_2 have been reported by Alterovitz and Gerlich (1969, 1970a) and by Gerlich (1968). These materials are hard; the micro-hardness of CaF_2, SrF_2, BaF_2, CdF_2 and PbF_2 has been reported by Rao and Sirdeshmukh (1983.)

X-ray studies by Weiss et al. (1957) and Togawa (1964) revealed that the CaF_2 crystal is built of ions with low density of electrons between them; the bonding is mainly ionic with no sign of covalency. Neutron diffraction studies of UO_2 have been performed at high temperatures to study the temperature variation of thermal vibrational amplitudes (Clausen et al. 1984). These studies have provided information about the anharmonicity of vibrations.

The dielectric constants of CaF_2, SrF_2 and BaF_2 have been measured by Lowndes (1969). The temperature and pressure variation of dielectric constants of the alkaline earth fluorides and PbF_2 was measuring by Samara (1976).

The fluorite structure has a simple but intense Raman spectrum which consists of a single line in the first order. The temperature variation of the wave length, intensity and line shape of the Raman lines in CaF_2, SrF_2, BaF_2, and PbF_2 has been studies by Elliott et al., (1978) at high temperatures. These studies have revealed the existence of a high degree of anharmonicity as well as disorder in these crystals at high temperatures.

The specific heats of several crystals with fluorite structure have been measured by Dworkin and Bredig (1968) and Derrington et al., (1976) over a wide range of temperature almost upto the melting point. The Debye temperatures have been calculated from the elastic constants. These results are complied by Hayes (1974) and by White (1980).

The lattice dynamics of fluorite type crystals has been investigated by several workers. Srinivasan (1958) and Ritz et al., (1961) used a rigid ion model with central forces. Denham et al., (1970) used a more refined model which employed a large number of parameters and a dynamical ionic charge. In a series of papers, Axe and co-workers (1965, a, b), (1966, a, b) used the shell model for several crystals with CaF_2 structure. Kuhner et al., (1972) employed a deformable shell model to study EuF_2 and $SrCl_2$.

Thermal expansion, being a property of technical as well as lattice dynamical interest, has received due attention. The thermal expansion of CeO_2, PrO_2, and ErO_2 was studies by Hati Baruo and Mahanta (1972) using the x-ray method. Momin and Karkhanawala (1978) determined the thermal expansion of UO2 and ThO2 at high temperatures by the x-ray method and calculated the Gruneisen constant. Benedict and Dufour (1980) studied the thermal expansion of AmO_2. This is an interesting system as the lattice constants are affected by self irradiation. Taylor (1984) has reviewed the thermal expansion results on the oxides with fluorites structure.

Among the fluorides with fluorite structure, CaF_2 has received maximum attention. Kopp (1852), Pfaff (1858) and Fizeau (1868) made measurements of thermal expansion over a limited temperature range near room temperature using mineral samples of fluorite. Sharma (1950) studies the temperature variation using the optical method. Krukowska – Flude and Niemyski (1967) determined the thermal expansion of CdF_2 using a dilatometer. Bailey and Yates (1967) made measurements at very low temperature employing an optical interferometer. Murat et al., (1971)_ made measurements of polycrystalline pellets of CaF_2, SrF_2 and BaF_2, using a dilatometer. Shaharbany et al., (1976) used a capacitance dilatometer to study the thermal expansion of CdF_2 at low temperatures. Rao and Maiti (1977) also used a simple capacitance technique to measure the thermal expansion of alkaline earth fluorides, but their measuring the thermal expansion coefficient of PbF_2 at low temperatures and reviewed the low temperature data on PbF_2 and alkaline earth fluorides. A method for measurements on the thermal expansion of small mineral crystals was proposed by Falzone an Stacey (1982). They studies SrF_2, among other crystals. Acluna and Ortiz (1985) measuring the thermal expansion of CdF_2 at elevated temperatures with an optical dilatometer.

Sirdeshmukh and Deshpande (1964) were the first to measure the lattice constants of CaF_2, SrF_2 and BaF_2 at elevated temperatures. In the same year, Batchelder and Simmons (1964) used the x-ray method to study the thermal expansion of CaF_2 at low temperatures. The lattice constants of PbF_2 were measured at temperatures. The lattice constants of PbF_2 were measure at temperatures upto the superionic region by Koto et al., (1980) using the x-ray method. However, they did not calculate the thermal expansion, nor did they give did they the lattice constant data in a retrievable form. Hazen and Finger (1981) carried out a unique x-ray measurement of temperature and pressure variation of lattice constants of CaF_2 and gave a polynomial in temperature as well as pressure. Recently Schumanmand Neumann (1984), Kommichau et al., (1986) and Neumann (1986) reported the lattice constant and thermal expansion of CaF_2, SrF_2 and BaF_2 over a wide temperature range. Unfortunately, these workers have made measurements at a very few temperatures and further the accuracy in determination of temperature and lattice constant is rather low; the error in thermal expansion is, consequently large.

II. The Properties Of Crystals With Pyrite Structure

The disulphide of Fe, Ni and Co form crystals with a cubic structure (FeS_2). These crystals are insoluble in water, occur as minerals and are stable over a high temperature range. FeS_2 occurs as the mineral pyrite in the form of well-formed single crystals of large dimensions (several mm). NiS_2 and CoS_2 also occur as minerals. Their crystal growth is difficult and extensive efforts (Ripley, 1972). Nickel et al., (1969a) determined the hardness of these crystals; the crystals are very hard. Nickel et al., (1969b) also recorded the infra-red spectrum and calculated the bond energies. Bhagavantham (1955) determined the elastic constants of FeS_2 over the temperature range 300-600 K.

There is very meager work on the thermal expansion of these crystals. Sharma (1951) determined the thermal expansion of FeS_2 at elevated temperatures using an optical interferometer. Straumanis et al., (1964) used the x-ray method to determine the thermal expansion coefficients of natural and synthetic samples of FeS_2 and CoS_2; but they covered a very limited temperature range near the room temperature. Chrystal (1965) determined the lattice constants of FeS_2 at elevated temperatures and calculated difference in the coefficients of thermal expansion obtained by Sharma on bulk samples and those obtained by him to the effect of thermally generated defects, Chrystal (1965) estimated a value of 0.312 eV for the energy of formation of defects; this is a very low value.

A critical examination of the existing work on thermal expansion of crystals with the fluorite and pyrite structures reveals the following features.
i) There is no data on the lattice constants of CdF_2 at elevated temperatures.
ii) There is no data on the thermal expansion of PbF_2 using the x-ray method.
iii) In the case of CaF_2, SrF_2 and BaF_2 there is difference between the results reported by Sirdeshmukh and Deshpande (1964) and the recent results by Neumann and co-workers. Also, the x-ray results differ from the results on bulk samples. Further, Bailey and Yates (1967) comment that the high temperature results of Sirdeshmukh and Deshpande (1964) do not form a smooth continuation of their low temperature results.
iv) In the case of FeS_2, there is a single report on the x-ray determination of thermal expansion, which has led to an abnormally low value for the formation energy of defects.

References

[1]   Acuna L A and Ortiz M F (1985) J. Phys. Chem. Solids, Vol. 46, 401.
[2]   Alterovitz S and Gerlich D (1969) Phys. Rev. 184, 999.
[3]   Alterovitz S and Gerlich D (1970a) Phys. Rev. 1, 2718.
[4]   Alterovitz S and Gerlich D (1970b) Phys. Rev. 1, 4136.
[5]   Anderson O L (1967) 1st International Conference of Thermal Expansion, 1967.
[6]   Askill J (1965) Phys. Stat Sol. 11, K49.
[7]   Axe J D Gaglianeolo J W and Seardfield J E (1965) Phys. Rev. 139, A. 1211.
[8]   Axe J D (1965) Phys. Rev. 139, A. 1215.
[9]   Axe J D and Pettit G D (1966) Phys. Rev. 151, 676.
[10]   Axe J D and Pettit G D (1966) J. Phys. Chem. Solids, 27, 621.
[11]   Bailey A C and Yates B (1967) Phil. Mag. 16, 1241.
[12]   Bailey A C and Yates B (1967) Proc. Phys. Soc.91, 390.
[13]   Batchelder D N and Simmons R O (1984) J. Chem. Phys. 41, 2324.
[14]   Bayer G (1972) J. Lesss Common Metals, 26, 255.
[15]   Bendict U and Dufour C (1980) Physica 102B, 303.
[16]   Bhagavanatam S (1955) Proc. Ind. Acad. Sci. XLI – 72.
[17]   Boehler R and Kennedy G C (1980) J Phys. Chem. Solids, 41, 1019.
[18]   Compbell W J (1962) Dept. of Interior, U.S. Bureau of Mins, RI 6115.
[19]   Chrystal R S B (1965) Trans Farad Soc. 512, 1811.
[20]   Clausen K, Hayes W, Hutchings M T, Macdonald J E,
[21]   Osborn R and Schnabel P (1984) Revu Phys. Appl. 19, 719.
[22]   Collins W C (1973) Phys. Stat Sol. (b) 56, 291.
[23]   Denham P, Field G R, Morse P L R and Wilkinson G R (1970) Proc. Roy. Soc. Lond. A. 317, 55.

[24] Derrington C E, Navrostsky A and Keefe M O (1976) Sol. State Comm. 18, 47.
[25] Deshpande V T and Suryanarayana S V (1969) Curr Sci (1969) 38, 489.
[26] Deshpande V T and Sirdeshmukh D B (1972) Act. Cryst. A 28, 94.
[27] Deus P, Neumann H, Kunn G and Hinze B (1983) Phys. Stat Sol (a) 80, 205.
[28] Dowrkin A S and Bredig M A (1968) J. Phys. Chem. Solids, 72, 1277.
[29] Elliot R J, Hayes W, Klepmann W G, Rushworth A J and Ryan J F (1978) Proc. R. Soc. Lond, A 360, 317.
[30] Fizeau (1868) Compt. Rend. 66, 1072.
[31] Falzone A J Stacey F D (1982) Phys. Chem. Min 8:212.
[32] Fullam H T (1972) Mat. Res. Bull. 7, 289.
[33] Geller S, Espinosa G P and Crandall P B (1969) J. Appl. Cryst. 2, 86.
[34] Gerlich D (1964a) Phys. Rev. 135, 1333.
[35] Gerlich D (1964b) Phys. Rev. 136, A. 1336.
[36] Gerlich D (1968) Phsy. Rev. 168 A. 947.
[37] Hanneman R E and Gatos H C (1965) J. App. Phys. 36, 1794.
[38] Harris P and Avarami L (1972) Technical Report No.4423, Picatinny Arsenal Dover NJ.
[39] Hati Barua and Mahantha P C (1972) Ind. J. Pure and Appl. Phys. 10, 599.
[40] Haussuhl S (1963) Phys. Stat. Sol. 3, 1072.
[41] Hayes W (1974) Crystals with Fluorite Structure (Clarendon Press, Oxford)
[42] Hazen R M and Finger L W (1981) J. Appl. Cryst. 14, 234.
[43] Herold A, Forsterling and Leinstuck K (1981) Cryst. Res. Tech. 16, 1137.
[44] Houska C R and Stein B A (1966) Acta Cryst. 21, 611.
[45] Hovi V and Pirinen J (1972) Ann. Acad. Sci. Fenni, A. 390, 3.
[46] Huffmann D R and Norwood M H (1960) Phys. Rev. 117, 709.
[47] Kachhava C M and Saxena S C (1965) Ind. J. Phys. 39, 145.
[48] Khan A A and Deshpande V T (1968) Acta Cryst. A. 24, 402.
[49] Khan A A (1974) Acta Cryst. A.30, 105.
[50] Kirby R K (1967) J. Res. Nat. Bur. Stand. A.71, 363.
[51] Kistaiah P, Venudhar Y C, Sathyanarayana Murthy K,
[52] Leela Iyengar and Krishna Rao KV (1981a) Pramana, 16, 281.
[53] Kistaiah P, Venudhar Y C, Sathyanarayanamurthy K. Leela Iyengar and Krishna Rao K V (1981b) J. Less. Comm. Met. 77, 9.
[54] Kistaiah P, Venudhar Y C, Sathyanarayanamurthy K. Leela Iyengar and Krishna Rao K V (1981c)   J. Phys. D 14, 457.
[55] Kittel C (1971) Introduction to Solid State Physics (John Wiley and sons, N.Y.)
[56] Knopoff L and Shapiro J N (1969) J. Geophys. Res. 74, 1439.
[57] Kommichau G, Neumann H, Schmitz W and Schumann B (1986) Cryst. Res. Techn. 21, 1583.
[58] Kopp (1852) Ann. Chim. Phys. 3, 340.
[59] Koto K, Schulz H and Huggins R A (1980) Solid State Ionics, 3/4 381.
[60] Krause A, Schafer H W and Helberg H W (1983) J. De. Physique, C_3 – 1429.
[61] Krishnan R S (1958) Progress in Crystal Physics, (S Viswanathan, Madras)
[62] Krishnan R S, Srinivasan R and Devanarayanan S (1979) Thermal Expansion of Crystals – (Pergmon Press, N.Y.)
[63] Krishna Rao K V, Nagender S V and Leela Iyengar J. Phys. Soc. Jpan (1967) 23, 1380.
[64] Krishna Rao KV and Leela Iyengar (1969) Curr. Sci. 38, 304.
[65] Krishna Rao K V, Nagender S V and Leela Iyengar (1970) J. Am. Cer. Soc.5., 124.
[66] Krishna Rao K V, Nagender S V and Leela Iyengar (1973) J. Appl. Cryst. 6, 136.
[67] Krishna Rao K V and Deshpande V T (1978) Thermal Expansion 6 – (Plenum Publishing Corpn. New York 10011).
[68] Lownder R P (1969) J. Phys. C. 2, 1595.
[69] Manasreh M O and Pederson D O (1984) Phy. Rev. B. 30, 3482.
[70] Manasreh M O and Pederson D O (1985) Phys. Rev. B. 31, 3960.
[71] Momin A C and Karkhanawala M D (1978) High Temp. Sci. 10, 45.
[72] Murat M and Chatelut F (1971) Ext. du. Bull. De la Soc. Chimique de. France, 49, 3101.
[73] Neumann H (1983) Cryst. Res. Technol. 18, K. 126.
[74] Neumann H, Deus P, Tomilson R D, Kuhn G and Hintze B (1984) Phys. Stat. So. (a) 84, 87.
[75] Neumann H, Kommichau G, Schmitz W and Schumann B (1986) J. Mat. Sci. Lett. 5, 1131.
[76] Nickel E H, Webster A H and Ripley L G (1969) Canad. Miner. 10, 773
[77] Nickel E H, Webster A H and Ripley L G (1969) Presented at the Annual Meeting of the Mineralogical Society of American, Atlantica City, N.J. Nov-12.
[78] Pfaff (1858) Pogg. Ann. 104, 182.
[79] Pathak P D and Vasavada N G (1972) Acta Cryst. Vol. A 28, 30.
[80] Pathak P D, Trivedi J M and Vasavad (1973) Acta Cryst. Vol. A 29, 477.
[81] Pandey R P and Pandey J D (1980) Ind. J. Pure and App. Phys. 18, 825.
[82] Plendl J N (1973) Phys. Status Solidi. B. 57, 187.
[83] Rao K V and Maiti J (1977) Ind. J. Pur. Appl. Phys. 15, 437.
[84] Rao B K and Sirdeshmukh D B (1980) Ind J Pure and Appl. Phys 18, 56.
[85] Rapp R R and Merchat H D (1973a) J. Appl. Phys. 44, No.9, 3919.
[86] Reeber R R and Kulp B A (1965) Trans of the Met. Soc. Of AIME, 23, 699.
[87] Reeber R R and Powell G W (1967) J. Appl. Phys. Vol. 38, No.4, 1531.
[88] Reddy B P N and Reddy P J (1973) Phys. Stat. Sol. (a) 17, 589.
[89] Rimai D S and Sladeck R J (1980) Phys. Rev. B 21, 843.
[90] Ripley L G (1972) Report R 237, Department of Energy Mines and Resurces, Ottawa.
[91] Reitz J R, Seitz R N and Ganberg R W (1961) J. Phys. Chem. Solids, 19, 73.
[92] Roberts R B, White G K and Sabine T M (1981) Aust. J. Phys. 34, 701.
[93] Samara G A (1976) Phys. Rev. B.13, 4529.
[94] Schumann B and Neumann H (1984) Crys. Res. Tech. 19, K 13.
[95] Shaner J W (1973) Phys. Rev. B. 7, 5008.
[96] Shaharabany D, Wolf M and Gerlich D (1976) J. Phys. Chem. Solids, 37, 577.

[97]   Sharma S S (1951) Proc. Ind. Acad. Sci. A 34, 72.
[98]   Sirdeshmukh D B J. Chem. Phys. 45, 2333.
[99]   Sirdeshmukh D B J. Appl. Phys. 38, 4083.
[100]   Sirdeshmukh D B and Deshpande V T (1964) Ind. J. Pure and Appl. Phys. 2, 405.
[101]   Sirdeshmukh D B and Rao B K (1972) J. Chem. Phys. 57.
[102]   Sirdeshmukh D B and Rao B K (1975) J. Phys. And Chem. Solids, 36, 395.
[103]   Slack G A and Bartram S F (1975) J. Appl. Phys. 46, 89.
[104]   Somi Reddy M and Suryanarayana S V (1983) J. Mat. Sci. Lett. 2, 171.
[105]   Somi Reddy M and Suryanarayana S V (1984) J. Mat. Scie. Lett. 3, 325.
[106]   Srinivasan R (1958) Proc. Phys. Lond. 72, 566.
[107]   Srivastava K K and Merchant H D (1973) J. Phys. Chem. Solids 34, 2069.
[108]   Straumanis M E, Armstrong G C and Chan S (1964) Am. Miner. 49, 206.
[109]   Suryanarayana S V and Deshpande V T (1978) Vistas in Molecular, Solid State and Biophysics.
[110]   Taylor D (1984) Br. Ceram Trans. J. 83, 32.
[111]   Testardi L R (1972) Phys. Rev. B. 4, 4342.
[112]   Togawa S (1964) J. Phys. Soc. Japan, 19, 1696.
[113]   Van Uitert L.G. Bryan H M, Lines M E, Guggenheim HS and Zydzik G (1977) Mat. Res. Bull. 12, 261.
[114]   Vetelino J F, Namjoshi K V and Mitra S S (1970) J. Appl. Phys. 41, 5141.
[115]   Vetelino J F, Namjoshi K V and Mitra S S (1970) Phys. Rev. B. 2, 2167.
[116]   Weiss A, Witte H and Wlfel E (1957) Z. Phys. Chem. 10, 98.
[117]   White G K (1965) Proc. R. Soc. A. 286, 204.
[118]   White G K (1980) J. Phys. Chem. Solid St. Phys. 13, 4905.
[119]   White G K and Collins J G (1972) Low Temp. Phys. Chem. Solids, 28, 1225.
[120]   Wong C and Schuele D E (1968) J. Phys. Chem. Solids, 29, 1309.
[121]   Yagi T (1978) J. Phys. Chem. Solids, 39, 563.