Elastic Constants of Strontium Fluoride Between 4.2 and 300°K

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(Received 15 July 1964)

The elastic constants of single-crystal SrF_2 have been determined over the temperature range 4.2–300°K, by an ultrasonic pulse-echo technique. The values of the elastic constants, extrapolated to 0°K, in units of 10^{11} dyn/cm², are: $c_{11}=12.88$, $c_{12}=4.748$, and $c_{44}=3.308$. From these values, a Debye temperature of 380°K is calculated for SrF_2 at 0°K. The elastic constants of SrF_2 are computed theoretically from a rigid-ion model, and the results are compared with the experimentally measured values. The elastic constants of SrF_2 are compared with those of the other alkaline-earth fluorides.

I. INTRODUCTION

THE properties of the alkaline-earth fluorides have been investigated extensively over the last years,[1,2] and the elastic constants of several of them have been measured.[3,4] The present report describes measurements of the elastic constants of SrF_2 over the temperature range 4.2-300°K. Since SrF_2 is an ionic material, its elastic constants can be computed theroetically from a simple lattice model, and these computed elastic constants can be compared with the experimental data, in order to examine the applicability of the theoretical model.

II. EXPERIMENTAL TECHNIQUE

The single crystal of SrF_2 was grown by pulling from the melt. After growth, it was annealed at 900°C for twenty hours in order to relieve the strains. The crystal thus obtained was optically clear, with most of the strain relieved.

Strontium fluoride crystallizes in the cubic system, and thus has three independent elastic constants, c_{11}, c_{12}, and c_{44}. These constants were determined by measuring the sound velocity in several different crystalline directions. Two sets of faces were ground on the crystal, one set corresponded to a (100) crystalline plane, while the other set to a (110) plane. Quartz crystal transducers, X and Y cut, of 15-Mc/sec fundamental frequency, were used for generating longitudinal and shear sound waves, respectively. The sound velocity was measured by a conventional pulse-echo technique, using unrectified pulses,[5] thus avoiding the necessity for the "time-of-flight correction." Over the range from room temperature to 78°K, "Nonaq" stopcock grease was used for bonding the transducer to the crystal, while from 78 down to 4.2°K, Dow Corning No. 200 silicone fluid, 1000-centistoke viscosity, was used as a bonding agent.

The elastic constants were determined from the measured sound velocities in five different modes of propagation. The latter were, a longitudinal, and a shear wave in the [100] direction, and a longitudinal, and two shear waves in the [110] direction, the latter being polarized in the [1$\bar{1}$0] and [001] directions respectively. From these five different velocities, the three elastic constants were computed by means of a least square fit. Based on an error of $\pm 0.2\%$ in the sound velocity, and judging by the scattering of the data, the error in the elastic constants is estimated as $\pm 0.2\%$.

III. RESULTS AND DISCUSSION

The measured values of the sound velocity, in the different crystalline directions, as a function of the temperature between 4.2 and 300°K, are shown in Fig. 1. The three elastic constants, c_{11}, c_{12}, and c_{44}, computed from the velocity versus temperature curves, are presented in Fig. 2. In Table I, the numerical values of the

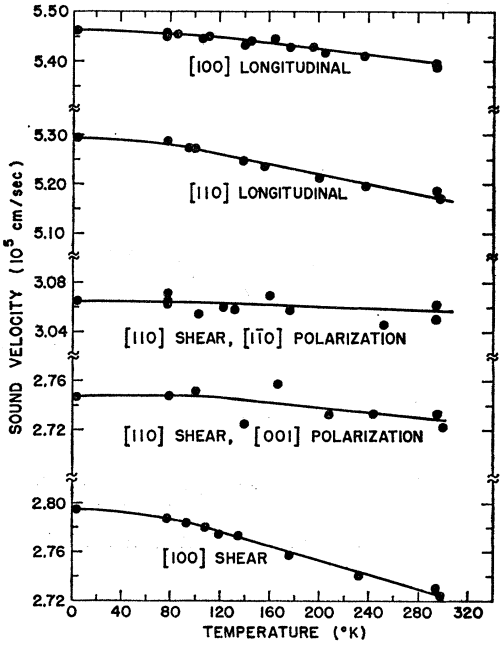

FIG. 1. The sound velocities in the different crystalline directions as a function of temperature for SrF_2.

[1] W. Kaiser, W. G. Spitzer, R. H. Kaiser, and L. E. Howarth, Phys. Rev. **127**, 1950 (1962).
[2] W. Low, in *Advances in Quantum Electronics*, edited by J. Singer (Columbia University Press, New York, 1962).
[3] D. R. Huffman and M. H. Norwood, Phys. Rev. **117**, 709 (1960).
[4] D. Gerlich, Phys. Rev. **135**, A1331 (1964).
[5] S. Eros and J. R. Reitz, J. Appl. Phys. **29**, 683 (1958).

TABLE I. The elastic constants and density of SrF_2 over the range 4.2-300°K.

T (°K)	ρ (g cm^{-3})	c_{11} (10^{11} dyn cm^{-2})	c_{12} (10^{11} dyn cm^{-2})	c_{44} (10^{11} dyn cm^{-2})
4.2	4.321	12.87	4.748	3.308
20	4.321	12.88	4.747	3.308
40	4.320	12.86	4.736	3.304
60	4.320	12.85	4.716	3.297
80	4.319	12.82	4.695	3.291
100	4.316	12.79	4.664	3.280
120	4.314	12.75	4.626	3.264
140	4.311	12.71	4.592	3.250
160	4.308	12.66	4.554	3.235
180	4.304	12.62	4.521	3.219
200	4.300	12.58	4.485	3.205
220	4.295	12.53	4.446	3.191
240	4.290	12.48	4.510	3.176
260	4.286	12.44	4.376	3.161
280	4.281	12.39	4.342	3.144
300	4.277	12.35	4.305	3.128

elastic constants together with the density ρ over the same temperature range are given. The values of the thermal expansion coefficient, as a function of temperature $\alpha(T)$, which are required in correcting for the changes in the path length and density between 4.2 and 300°K, were estimated from the corresponding data for CaF_2. Since the room-temperature values of α for both materials[6,7] differ by only 5% ,and as both materials have the same crystalline structure, it was assumed that the temperature dependence of $\alpha(T)$ is the same for both CaF_2 and SrF_2. The values of $\alpha(T)$ for SrF_2 were then computed from those of CaF_2, by multiplying the latter by the ratio of the room temperature values of α for the two materials. In the temperature range 4.2-78°K, where no experimental α data for CaF_2 are available, they were computed from the specific heat data[3,8] and the Grüneisen relation.[9] Although this procedure is probably a rough estimate only, it is sufficient for the present prupose, since the correction due to thermal expansion is quite small.

As can be seen from Fig. 2, c_{11} changes by about 4%, c_{12} by 10%, and c_{44} by 6% between 4.2 and 300°K. It is interesting to note that although SrF_2 occupies an intermediate position between CaF_2 and BaF_2, the variation of c_{11} over the above temperature range is smaller in the case of SrF_2 than for both[3,4] CaF_2 and BaF_2.

The elastic constants of CaF_2 have been calculated theoretically,[10] assuming a rigid ion model and representing the repulsive overlap energy between the cation and anion by a term proportional to r_0^{-10}, where r_0 is the lattice constant. The theoretical elastic constants of SrF_2 were computed in an analogous manner, and the results, together with the room-temperature experimental values are shown in Table II. As can be seen, there is good agreement between the experimental and theoretical values for c_{11} and c_{12}, while the agreement is poorer for c_{12}-c_{44}. This is also the case for calcium fluoride,[3] and is not surprising, since the theoretical values of c_{11} and c_{12} have been evaluated from the experimentally measured bulk modulus, and principal Raman line.[11] On the other hand, c_{12}-c_{44} is determined from the difference between two large terms and thus includes a larger error. It can therefore be deduced that the rigid ion model is a fairly good approximation for the SrF_2 lattice.

TABLE II. Comparison of the experimental and theoretical values of the elastic constants (in units of 10^{11} dyn cm^{-2}).

	c_{11}	c_{12}	$c_{12}-c_{44}$
Experimental	12.35	4.305	1.177
Theoretical	12.7	3.97	0.56

Utilizing the procedure of Marcus and Kennedy,[12] a Debye temperature of 380°K at 0°K, is calculated from the values of the elastic constants extrapolated to 0°K. Since specific heat data for SrF_2 are not available, no comparison with the Debye temperature determined from such data can be made.

According to the classical theory of the ionic lattice,[13] the bulk modulus K is given by

$$K=[(n-1)A/9\delta](q^2/r_0^4), \quad (1)$$

where A is the Madelung constant, δ a constant characteristic of the lattice type, n the exponent of r_0

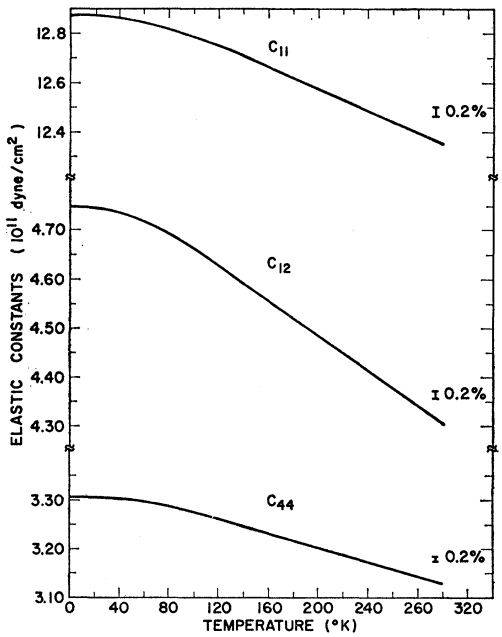

FIG. 2. The elastic constants of SrF_2 as a function of temperature.

[6] S. Valentiner and J. Wallot, Ann. Physik **46**, 837 (1915).
[7] R. J. Paff (private communication).
[8] S. Todd, J. Am. Chem. Soc. **71**, 4115 (1949).
[9] N. F. Mott and H. Jones, *Theory of Metals* (Clarendon Press, Oxford, England, 1936).
[10] R. Srivinasan, Proc. Phys. Soc. (London) **72**, 566 (1958).
[11] A. V. R. Warrier and R. S. Krishann, Naturwissenschaften **51**, 8 (1964).
[12] P. A. Marcus and A. Kennedy, Phys. Rev. **114**, 459 (1959).
[13] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. 2.

TABLE III. The reduced bulk modulus for the three alkaline-earth fluorides.

	CaF_2	SrF_2	BaF_2
K*	34.0	34.4	36.3

in the repulsive lattice energy term, and q the electronic charge. Since all the three alkaline-earth fluorides, CaF_2, SrF_2, and BaF_2 have the same crystalline structure, A and δ are the same for all three. It is also reasonable to assume that the value of n is the same for all the three. If this model, therefore, is rigorously applicable to all three alkaline earth fluorides, then the reduced bulk modulus K^*, defined as $K/(q^2r_0^{-4})$, would be equal for all three materials. In Table III, K^* for the three alkaline-earth fluorides is shown. As can be seen, K^* is nearly equal for CaF_2 and SrF_2, while for BaF_2 the discrepancy is much larger. This is not surprising, since the rigid ion model is least applicable to barium fluoride.[4]

ACKNOWLEDGMENTS

The author wishes to express his indebtedness to H. E. Temple for growing the SrF_2 single crystal, to R. T. Smith for the x-ray orientation of the crystal, and to R. J. Paff for the thermal expansion coefficient measurements.

PHYSICAL REVIEW VOLUME 136, NUMBER 5A 30 NOVEMBER 1964

Electron Spin Resonance of Concentrated Copper Phthalocyanine Crystals

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(Received 23 June 1964)

An electron-spin-resonance study of pure copper phthalocyanine single crystal reveals a highly anisotropic environment. There are strong exchange and dipolar interactions between equivalent sites. However, the exchange interactions between the two nonequivalent sites are small enough to permit detection and separation of the two individual resonances. Values of g and the linewidth have been measured as a function of angle in the three crystallographic planes. The variation of ΔH is discussed in terms of the exchange narrowing, exchange broadening, dipolar broadening, and hyperfine interaction.

I. INTRODUCTION

ELECTRON-spin-resonance (ESR) measurements on single crystals of copper phthalocyanine magnetically diluted in metal-free phthalocyanine have been reported previously.[1] ESR spectra of Cu^{2+} ion in a dilute crystal, in which the interactions between neighboring ions are negligible, consists of four copper hyperfine lines. Each of the copper lines is further split into nine lines by the nitrogen nuclear interaction.[1] In this paper we report measurements on undiluted copper phthalocyanine crystals, which were found to have extremely anisotropic magnetic properties.

In the copper complex the spin-lattice relaxation time is long compared with the spin-spin relaxation time. Therefore, we find no temperature dependence of the linewidth in our analysis, and consequently we concern ourselves solely with the ion-ion interactions and ignore the spin-lattice interaction. In concentrated paramagnetic crystals, the magnetic interactions between neighboring ions cause considerable overlapping of the hyperfine lines, and only one broad resonance line is usually found. The breadth of the resonance line depends on the relative magnitude of the spin-spin dipolar interaction, exchange narrowing between equivalent ions, and exchange broadening between nonequivalent ions. Although the physical nature of these interactions is understood, complete theoretical and quantitative treatment is lacking at present. Nevertheless, it is of interest to study these interactions by investigating the angular dependence of the ESR spectra and comparing it with computed theoretical curves.[2-4]

II. CRYSTALLOGRAPHY

The phthalocyanine compounds form a monoclinic series, in which the crystallographic axes a, b, and c are closely related by the ratio 4:1:3. The b axis is normal to the ac plane, and the a axis makes an angle of 120°36′ with the c axis in the copper crystal. Robertson[5] has determined the crystal dimensions of the copper phthalocyanine by x-ray measurements. The cell dimensions of the monoclinic crystal are $a=19.6$ Å, $b=4.79$ Å, and $c=14.6$ Å, and $\beta=120°36'$. The unit cell contains two molecules with parameters (0,0,0) and $(\frac{1}{2},\frac{1}{2},0)$. One molecule is translated into the second by a screw rotation of 180° about the b axis. The two mole-

[1] S. E. Harrison and J. M. Assour, J. Chem. Phys. **40**, 365 (1964).

[2] D. M. S. Bagguley and J. H. E. Griffiths, Proc. Roy. Soc. (London) **201**, 366 (1950).

[3] H. Kamagai, K. Ôno, I. Hayashi, H. Abe, and J. Shimada, J. Phys. Soc. (Japan) **9**, 369 (1954).

[4] B. Bleaney, R. P. Penrose, and B. I. Plumpton, Proc. Roy. Soc. (London) **A198**, 406 (1949).

[5] J. M. Robertson, J. Chem. Soc. **1935**, 615 (1935); 1105 (1935).