small $J' \sim 0.01J$ raises the ordering temperature to about 20% of its value for the isotropic case $J = J'$.

[96] L. Onsager, Phys. Rev. 65, 117 (1944).

[97] The error limits given here and for other energies in this section correspond to the maximum ranges allowed by the uncertainties for the J's given in Table III. In comparing energies of different states one must take account of correlations between the different expressions, which will generally tend to reduce the uncertainties in the differences. Also, the relatively large uncertainty quoted for J_3 is probably too pessimistic, since it would seem most probable that J_3 is in fact very close to zero. In making comparisons it is therefore probably best to concentrate on the actual values, even though the quoted ranges of values are allowed by the available parameters.

[98] The summation in this calculation has to be performed with some care since the energies of different sections of the two spirals will vary with the local orientation of the spins (and not only with the *relative* phase angle which remains constant). In practice we took account of this by carrying out an explicit double sum over a large number of spins in both the central spiral (a_n) and the neighboring spirals (b_n, c_n, etc.) for different fixed values of θ. Possible refinements of this procedure are evident, but we shall defer them to a later more detailed study.

[99] See, for example, B. R. Cooper, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1968), Vol. 21, p. 393.

[100] T. Nagamiya, K. Yosida, and R. Kudo, Advan. Phys. 4, 1 (1955).

[101] The form of the exchange interactions in the Hamiltonian used by Marquard is $-2\sum_{i>j} J'_{ij} \vec{S}_i \cdot \vec{S}_j$ (Ref. 47). Thus our J_{ij} is equal to $-2J'_{ij}$. This appears as different factors in our expressions for the expansion coefficients compared to those used by Marquard.

[102] A description of the programs used may be obtained from the authors on request.

[103] The numerical values for the individual sums are given in Ref. 6.

[104] J. W. Stout and E. Catalano, J. Chem. Phys. 23, 2013 (1955).

[105] M. Blackman, in *Handbuch der Physik*, edited by S. Flügge (Springer, Berlin, 1955), Vol. 7, p. 325.

[106] Using the relation $C_L/R = 234\ (T/\Theta_D)^3 \simeq 3.4 \times 10^{-5} T^3$.

[107] Comparison of similar estimates of lattice specific heats for other rare-earth hydroxides, (Ref. 4), revealed no systematic trend according to the atomic masses. In fact, it was found that $a[R(OH)_3] \simeq \beta a[La(OH)_3]$ with $\beta = 1.04$, 0.87, 0.97, and 1.07 for R = Nd, Gd, Tb, and Er, respectively.

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Third-Order Elastic Constants of $RbMnF_3$ †

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The complete set of six third-order elastic constants of $RbMnF_3$ has been determined from measurements of hydrostatic-pressure and uniaxial-compression derivatives of natural sound velocities. Measurements were made at room temperature using an ultrasonic pulse-superposition technique. The results are $c_{111} = -18.4$, $c_{112} = -2.4$, $c_{123} = +0.4$, $c_{144} = -0.6$, $c_{155} = -1.8$, and $c_{456} = -0.5$ in units of 10^{12} dyn/cm². The results are interpreted to mean that the third-order elastic constants are predominantly determined by the Mn-F interaction. The significance of this for the mechanics of $RbMnF_3$ is discussed.

I. INTRODUCTION

Ultrasonic studies of rubidium manganese trifluoride ($RbMnF_3$) have been reported recently by several authors. Properties studied include second-order elastic constants (SOEC) and their temperature dependence,[1] magnetoelastic coupling,[2,3] nuclear acoustic resonance,[4,5] nuclear magnetic resonance,[6] and ultrasonic attenuation near the Néel temperature.[7,8] Results of the first study of the nonlinear elastic properties of $RbMnF_3$, namely, the third-order elastic constants (TOEC), are reported here.

$RbMnF_3$ belongs to the $Pm3m = O_h^1$ space group and has the familiar perovskite-type cubic crystal structure. All O_h point groups have six independent TOEC.[9] These constants were determined directly from measurements of the hydrostatic-pressure and uniaxial-compression derivatives of natural sound velocities in a single crystal. This is believed to be only the second report of a complete set of TOEC for a perovskite-type crystal structure; TOEC of $SrTiO_3$ were previously obtained by combining the pressure-derivative data of Beattie and Samara[10] with the second-harmonic-generation data of Mackey and Arnold.[11]

II. EXPERIMENTAL PROCEDURE AND RESULTS

A $RbMnF_3$ single crystal was obtained from Isomet Corp., Oakland, N. J., in the shape of a 1-cm cube. Faces of the cube were near $\{001\}$, $\{110\}$, and $\{1\bar{1}0\}$ planes; misorientations of the respective faces were found to be 2°, 3°, and 6° by Laue back-reflection photographs. Opposite faces of the sample were flat and parallel within 200 ppm. To facilitate handling, reduce attenuation, and suppress dislocation effects during uniaxial compression, the crystal was γ irradiated with a dosage of $\sim 10^5$ R.

Sound velocities and their stress derivatives were measured by a pulse-superposition method[12,13] using an improved detection system developed by Holder.[14] The directly measured quantity was the relative change of the natural velocity $w = 2L_0/t$, where L_0 is the unstressed path length and t is the round-trip transit time. An ultrasonic frequency of 10 MHz was used. Quartz transducers were attached to the sample with Non-Aq stopcock grease. Phenyl salicylate (salol) was also used as a bonding agent during measurements of the hydrostatic-pressure derivatives of the longitudinal elastic constants.

To determine TOEC from stress derivatives of sound velocities requires knowing the SOEC. The particular orientation of the sample permitted measurement of four combinations of SOEC, namely, c_{11}, c_{44}, $c' = \frac{1}{2}(c_{11} - c_{12})$, and $c_L = c_{11} + c_{44} - c'$. Preliminary measurements were made and found to be within 1% of the SOEC results of Melcher and Bolef.[1] Since the primary object of the present study was the relative change of the SOEC rather than their absolute values, the SOEC results of Melcher and Bolef were adopted.

Temperature derivatives of the natural sound velocities were measured so that velocities could be normalized to a standard temperature 22.000 °C. Temperatures were measured with Chromel-Constantan thermocouples, and changes could be determined to a mdeg. Results for the temperature derivatives obtained from measurements over a 2 °C interval near room temperature are given in Table I. Also tabulated are the temperature derivatives of the SOEC c. These derivatives were obtained by considering the SOEC to be functions of temperature T and pressure P. Then

$$\frac{\partial}{\partial T}(\ln c)_P = -\alpha + 2\frac{\partial}{\partial T}(\ln w)_P, \qquad (1)$$

where α is the linear thermal-expansion coefficient. For $RbMnF_3$, $\alpha = 0.19 \times 10^{-4}\,°C^{-1}$.[15] The errors indicated in the second and third columns of Table I are the standard deviations arising from a linear least-squares analysis of the velocity data. Only three of the temperature derivatives are independent since

$$\frac{\partial}{\partial T}(c_L)_P = \frac{\partial}{\partial T}(c_{11} + c_{44} - c')_P. \qquad (2)$$

A general least-squares analysis was used to obtain a self-consistent set of temperature derivatives; these are shown in the fourth column of Table I, and the errors there indicate the consistency of the data. Present results agree well with those of Melcher and Bolef.[1]

TABLE I. Logarithmic temperature derivatives of the natural velocities and of the SOEC of $RbMnF_3$ at 22 °C. Entries are in units of $10^{-4}\,°C^{-1}$.

		$\frac{\partial}{\partial T}(\ln c)_P$		
c	$\frac{\partial}{\partial T}(\ln w)_P$	Directly measured	Least-squares results	Melcher and Bolef
c_{11}	-1.59 ± 0.01	-3.37 ± 0.02	-3.58 ± 0.21	-3.49 ± 0.08
c_{44}	-0.31 ± 0.01	-0.81 ± 0.02	-0.87 ± 0.29	-0.89 ± 0.02
c'	-2.75 ± 0.03	-5.69 ± 0.06	-5.62 ± 0.29	-5.85 ± 0.10
c_L	-1.06 ± 0.01	-2.31 ± 0.02	-2.11 ± 0.26	···

Both hydrostatic-stress and uniaxial-stress derivatives of the natural sound velocities were measured. Hydrostatic stresses were obtained using a vessel pressurized with nitrogen gas; pressure was measured with a Heise Bourdon gauge. A heater coil in the pressure vessel was used to control temperature. The hydrostatic-stress range was 0–50 kg/cm². Uniaxial compressive stresses were obtained with a Tinius Olsen universal testing machine. To promote uniform compression, the crystal was placed between indium shims and the stress was applied through a ball joint. The uniaxial-stress range was 4–12 kg/cm².

The nine uniaxial and four hydrostatic experiments used to determine the six TOEC are listed in Table II. For each measurement the directly measured quantity is $(\partial/\partial P)(\ln w)_{T,P=0}$. It can be easily shown that

$$\frac{\partial}{\partial P}(\rho_0 w^2)_{T,P=0} = 2c\frac{\partial}{\partial P}(\ln w)_{T,P=0}, \qquad (3)$$

where c is the appropriate SOEC and ρ_0 is the mass density of the unstressed material. The pressure derivatives of $\ln w$ and of $\rho_0 w^2$ are listed in Table II for each measurement; the corresponding errors represent the range of the measured values. The explicit relations between the measured quantities $(\partial/\partial P)(\rho_0 w^2)_{T,P=0}$ and the SOEC and TOEC have been given by Thurston and Brugger.[16]

The results of measurements 10–13 were used to determine the hydrostatic-pressure derivatives of the SOEC. These were obtained from the relation

$$\left(\frac{\partial c}{\partial P}\right)_{T,P=0} = \frac{\partial}{\partial P}(\rho_0 w^2)_{T,P=0} + \frac{c}{3B^T}, \qquad (4)$$

where B^T is the isothermal bulk modulus, $B^T = \frac{1}{3}(c_{11}^T + 2c_{12}^T)$. Here $\partial c/\partial P$ means $\partial(\rho v^2)/\partial P$, where ρ is the density and v is the velocity. No distinction is made here between isothermal and adiabatic moduli. A calculation showed that isothermal and adiabatic compressibilities differed by less than 1%. Only three of the hydrostatic measurements are independent since

TABLE II. Results for sound-velocity stress derivatives.

Expt. no.	Propagation direction	Polarization direction	Stress direction	c	$\frac{\partial}{\partial P}(\ln w)_{T,P=0}$ (10^{-12} dyn^{-1} cm^2)	$\frac{\partial}{\partial P}(\rho_0 w^2)_{T,P=0}$ (dimensionless)
1	[110]	[110]	[001]	c_L	-0.95 ± 0.22	-2.12 ± 0.49
2	[110]	$[1\bar{1}0]$	[001]	c'	-0.92 ± 0.03	-0.69 ± 0.02
3	[110]	[001]	[001]	c_{44}	$+0.61\pm0.01$	$+0.39\pm0.01$
4	[001]	[001]	[110]	c_{11}	-1.02 ± 0.20	-2.39 ± 0.47
5	[001]	]110]	[110]	c_{44}	$+0.54\pm0.02$	$+0.35\pm0.01$
6	[001]	$[1\bar{1}0]$	[110]	c_{44}	-0.38 ± 0.01	-0.24 ± 0.01
7	[110]	[110]	$[1\bar{1}0]$	c_L	$+0.47\pm0.06$	$+1.05\pm0.13$
8	[110]	$[1\bar{1}0]$	$[1\bar{1}0]$	c'	$+2.08\pm0.05$	$+1.56\pm0.04$
9	[110]	[001]	$[1\bar{1}0]$	c_{44}	-0.52 ± 0.05	-0.33 ± 0.03
10	[001]	[001]	hydro.	c_{11}	$+4.01\pm0.39$	$+9.42\pm0.92$
11	[001]	any ⊥ [001]	hydro.	c_{44}	$+0.91\pm0.02$	$+0.58\pm0.01$
12	[110]	[110]	hydro.	c_L	$+2.95\pm0.12$	$+6.59\pm0.27$
13	[110]	$[1\bar{1}0]$	hydro.	c'	$+5.03\pm0.15$	$+3.78\pm0.11$

$c_{11}=1.174\times10^{12}$ dyn/cm^2, $c_{44}=0.3193\times10^{12}$ dyn/cm^2,
$c'=0.3763\times10^{12}$ dyn/cm^2, $c_L=1.117\times10^{12}$ dyn/cm^2

$$\left(\frac{\partial c_L}{\partial P}\right)_{T,P=0}=\frac{\partial}{\partial P}(c_{11}+c_{44}-c')_{T,P=0}\,. \tag{5}$$

A self-consistent set of pressure derivatives was obtained from a general least-squares analysis of the hydrostatic data. These results are given in Table III along with the errors indicating the consistency of the measurements.

Salama and Alers[17] suggested that comparing uniaxial and hydrostatic data indicates whether dislocations contribute to the apparent velocity change. Uniaxial stresses can move dislocations while hydrostatic stresses cannot. The hydrostatic measurements yielded three combinations of TOEC, namely, $(c_{111}+2c_{112})=-23.7\pm0.4$, $(c_{144}+2c_{155})=-3.8\pm0.1$, and $(2c_{112}+c_{123})=-3.0\pm0.8$, in units of 10^{12} dyn/cm^2. From the nine uniaxial measurements, a complete set of six TOEC was determined and these three linear combinations were calculated. The uniaxial results were $(c_{111}+2c_{112})=-19.2\pm0.3$, $(c_{144}+2c_{155})=-3.3\pm0.1$, and $(2c_{112}+c_{123})=-3.0\pm0.2$, in units of 10^{12} dyn/cm^2. Agreement between the two sets indicates that dislocations did not contribute significantly to the measured uniaxial-stress derivatives. Other effects also undoubtedly contributed to the small uniaxial-hydrostatic discrepancy, notably crystal misorientation and nonuniaxial loading due to friction between the crystal and the shims.

The hydrostatic and uniaxial data were combined to obtain a self-consistent set of TOEC. The results are given in Table IV along with the standard deviations arising from the least-squares analysis; these deviations indicate the over-all consistency of the combined data.

III. DISCUSSION

The elastic anisotropy of $\mathrm{RbMnF_3}$ is not strongly demonstrated by the SOEC, since $c_{44}/c'=0.85$. However, the temperature and pressure derivatives of the SOEC clearly indicate a higher degree of anisotropy: $(\partial c_{44}/\partial T)/(\partial c'/\partial T)=0.13$ and $(\partial c_{44}/\partial P)/(\partial c'/\partial P)=0.19$. In addition the isotropy ratios for the TOEC are found to be

$$(c_{123}+6c_{144}+8c_{456})/c_{111}=0.39, \tag{6}$$

$$(c_{123}+2c_{144})/c_{112}=0.33, \tag{7}$$

$$(c_{144}+2c_{456})/c_{155}=0.89; \tag{8}$$

for a perfectly isotropic material the above three ratios should equal unity.[16]

The only other perovskite-type crystal for which

TABLE III. Hydrostatic-pressure derivatives of the SOEC of $\mathrm{RbMnF_3}$.

c	$\left(\frac{\partial c}{\partial P}\right)_{T,P=0}$
c_{11}	10.19 ± 0.19
c_{44}	0.75 ± 0.07
c'	3.95 ± 0.08
c_L	6.99 ± 0.22

TABLE IV. TOEC of $\mathrm{RbMnF_3}$ in units of 10^{12} dyn/cm^2.

$c_{111}=-18.4\pm0.4$
$c_{112}=-2.4\pm0.2$
$c_{123}=+0.4\pm0.5$
$c_{144}=-0.6\pm0.3$
$c_{155}=-1.8\pm0.1$
$c_{456}=-0.5\pm0.1$

TOEC data are now available is $SrTiO_3$.[10,11] A strong correspondence exists between the elastic constants of $RbMnF_3$ and $SrTiO_3$. If a scaling factor is chosen such that c_{11} is the same for both materials, then all other elastic constants with the exception of c_{44} and c_{144} are also the same within experimental errors.

The results may be given a simple interpretation without any detailed calculations by use of an argument given by Hiki and Granato.[18] They found that for the fcc metals Cu, Ag, and Au, the TOEC tended to satisfy Cauchy relations ($c_{112}=c_{155}$ and $c_{123}=c_{144}=c_{456}$) much more nearly than did the SOEC. In addition, they found that $c_{112}\simeq \frac{1}{2}c_{111}$ and $c_{123}\simeq 0$. This is the pattern that would be expected for nearest-neighbor contributions for the fcc structure Long-range forces have a dominant influence on the energy of a solid, but become relatively less and less influential as one goes to higher derivatives of the energy (higher-order elastic constants). If it is supposed that short-range forces predominate for TOEC, the observed pattern is explained and the relative values of the TOEC are determined primarily by the relative geometric arrangement of the closest ions.

The unit cell of $RbMnF_3$ may be visualized as a simple cube with Rb ions at the corners, F ions at the face centers, and a Mn ion at the body center. The closest ions are the Mn-F pairs separated by distances of $\frac{1}{2}a$. The next closest are Rb-F and F-F pairs at distances of $\frac{1}{2}a\sqrt{2}$. For the Mn-F pairs, the nearest-neighbor arrangement is the same as for NaCl, for which the expected pattern is $c_{111}\neq 0$, all other $c_{ijk}=0$. To a first approximation, this is the pattern found in the present measurements. Different relative values are expected for the other ion pairs. Tables giving the relative values to be expected for different structures have been given and discussed by Holder and Granato.[19] The results for $RbMnF_3$ can then be simply interpreted as arising mainly from the Mn-F short-range repulsive interaction.

The significance of this result lies in the fact that this measurement focuses on the only interaction in this material that is difficult to obtain otherwise, presenting a unique opportunity to obtain a rather complete analysis of the mechanics of a perovskite structure. That is, information about the remaining short-range interactions between Rb-F and F-F should be obtainable by analysis of nearest-neighbor and next-nearest-neighbor contributions to the SOEC and TOEC of RbF. This possibility is also unique to the NaCl structure.[19,20] For example, c_{112} and c_{155} are unaffected by nearest-neighbor interactions and c_{123}, c_{144}, and c_{456} are unaffected by both nearest-neighbor and next-nearest-neighbor interactions. These interactions, together with Coulombic, van der Waal, and thermal-vibration contributions, undoubtedly account for the small deviations from the simple NaCl-type pattern observed for $RbMnF_3$. These calculations will be reported at a later date.

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