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RESONANCE ABSORPTION OF GAMMA QUANTA IN BARIUM, STRONTIUM, AND CALCIUM STANNATE

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The parameters of the resonance absorption of the 23.8-keV γ quanta emitted by Sn^{119*} were measured over the temperature range from 78 to 1020°K for the stannates of barium, strontium and calcium, which all have a perovskite structure. The temperature dependences of the probability for recoilless absorption and of the position of the resonance were studied. A similar characteristic variation of the width with temperature was found for all the compounds. For barium and strontium stannate we studied the temperature variation of the unit cell size in the temperature intervals 293—893 and 293—843°K, respectively. The effects of differences in atomic masses and parameters of the unit cell on the measured quantities are discussed, as well as a possible mechanism for the change in the width and shape of the absorption spectrum.

INTRODUCTION

EARLIER[1] we investigated the temperature dependence of the parameters of the resonance absorption of the 23.8-keV γ rays from Sn^{119*} in a crystal of SnO_2. It was found that with increasing temperature the width of the observed spectrum increases, while the probability f' for recoilless absorption drops very slowly.

In the present work we have made a similar study for crystals of $BaSnO_3$, $SrSnO_3$ and $CaSnO_3$. As the experiments showed, in these compounds f' remains sizable even at high temperatures, which allows measurements over a wide temperature range. The stannates listed all have the perovskite structure. Consequently they are convenient material for studying the effect on the resonance absorption of γ quanta of the difference in the masses of the alkaline earth ions of barium, strontium and calcium, as well as the difference in the symmetries and parameters of their unit cells.

These compounds are good dielectrics and are used in high frequency engineering.[2] However, their dielectric constant is still quite a bit lower than for the familiar ferro- and antiferroelectrics ABO_3 with the perovskite structure, which are characterized by the presence of comparatively high internal electric fields E (and field gradients) at the positions of the ions, in particular at the positions of the ions of B.[3-6] In contrast to this, the available structure data allow one to conclude that there is almost exactly the reverse picture in the stannates; at the centers of gravity of the B type ions (Sn) the field E is zero, and the gradients are also zero there. Starting from the possible difference in the distribution of internal fields in the stannates and the perovskite ferro- and antiferroelectrics, one can also explain the difference in their dielectric properties. For this the results of the study of resonance absorption of γ rays are very important, since they give independent information about the field gradients at the position of the tin ions.

CONDITIONS OF PREPARATION AND CHARACTERISTICS OF SAMPLES

The stannates of barium, strontium and calcium were obtained by the standard ceramic technique, by repeated roasting in an air atmosphere. The starting materials were the carbonates of barium, strontium and calcium, and tin dioxide, type ChDA (pure for analysis). The weighed-out materials were carefully mixed, pressed and fired first at T = 1250°C, being kept at the top temperature for 2 hrs. After this they were repeatedly ground and pressed and then given a final roasting at 1350—1400°C for 1—1.5 hrs. The x-ray analysis showed that the samples were single-phase. At room temperature $BaSnO_3$ has a cubic unit cell with period a = 4.114 Å. The patterns of the samples of $SrSnO_3$

and $CaSnO_3$ showed, in addition to the strong main lines, some weak lines[4,5] indicating the presence of superstructure in these compounds. The period of the pseudocubic subcell of $SrSnO_3$ was $a = 4.033$ Å, while the parameters of the distorted monoclinic subcell of $CaSnO_3$ were $a = c = 3.953$ Å, $b = 3.941$ Å $\beta = 91°31'$. The x-ray data found for all the stannates are in extremely good agreement with the literature values: for $SrSnO_3$ cf. [7], for $BaSnO_3$ and $CaSnO_3$ cf., for example, [8].

EXPERIMENT AND RESULTS

We used the technique and equipment described earlier.[1] In the experiments the source of $Sn^{119*}O_2$ (8 mg/cm^2) was at room temperature, while the absorber temperature varied from 78 to 1020°K. The absorbers were prepared by pressing powders of the stannates in a mixture with beryllium oxide.

At all temperatures the spectrum was a single broadened line. As an example, Fig. 1 shows the observed half-widths for absorbers of $SrSnO_3$ of different thickness. Within the experimental error, the points for a fixed temperature fall on a straight line. The half-widths extrapolated to zero absorber thickness, Γ_{ext}, are shown in Fig. 2. The values of Γ_{ext} exceed twice the natural width (0.62 mm/sec) and show a nonmonotonic temperature dependence: with increasing temperature Γ_{ext} first falls, and then, starting at $T \approx 650$°K, increases. A similar situation occurs for $BaSnO_3$ and $CaSnO_3$. The large widths of the measured spectra are due to broadening of both the emission and absorption lines. It was shown in [1] that the emission line from SnO_2 is close to the dispersion shape at room temperature, with a width of 0.62 mm/sec. On this assumption we calculated the dependence of the maximum absorption ϵ_0 and the width Γ_{obs} of the observed spectrum on the effective thickness C_A of the absorber for two different forms of the absorption line: a doublet structure and a dispersion shape with arbitrary width. The method of computation is described in several papers.[9,1] An important result of the computation is that for the same value of Γ_{ext} the slope of the Γ_{obs} vs. C_A curves is much less for the doublet structure than for the dispersion distribution. From this one can conclude that at temperatures $T \lesssim 500$°K the absorption line in these compounds has a doublet structure, while at high temperatures one sees a deviation from the doublet structure and an approach to the dispersion distribution. These facts show that at least two competing factors influence the shape of the absorption spectrum.

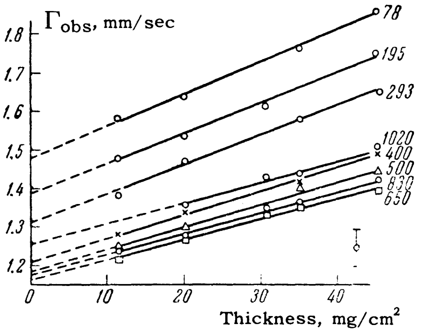

FIG. 1. Dependence of observed half-widths on $SrSnO_3$ absorber thickness for different temperatures (°K).

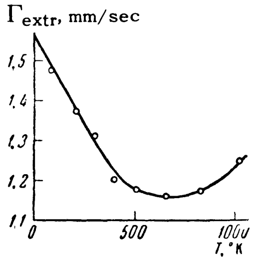

FIG. 2. Temperature dependence of width of spectrum extrapolated to zero absorber thickness.

Figure 3 shows the temperature dependence of the factor Z ($f' = e^{-Z}$) for the three compounds.

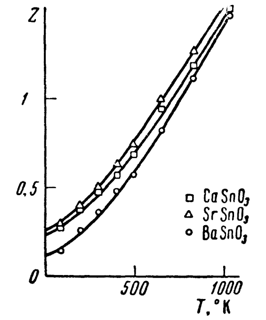

FIG. 3. Temperature dependence of $Z(f' = e^{-Z})$.

To determine Z we used the characteristics of the SnO_2 source which were found earlier.[1] At all temperatures the value of Z was smaller for $BaSnO_3$ than for $SrSnO_3$ and $CaSnO_3$. The values found for f′ at 78°K and at room temperature are considerably larger than those given in [10]; the reason for this is that in treating the data in [10] the broadening of the emission and absorption lines was not taken into account.

The results of measurements of the temperature shift are shown in Fig. 4. The shift values, determined from the asymmetry of the spectrum about the zero velocity, are given to an accuracy of 0.01 mm/sec. We see that the curve for $CaSnO_3$ runs lower than the curve for $BaSnO_3$ and $SrSnO_3$. This shows that the chemical shift for the first compound is different from the shift for the other two.

In order to study the possible effect of structure on the characteristic temperature variations of the

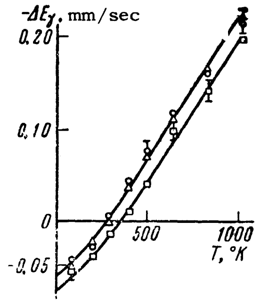

FIG. 4. Temperature shift of absorption line in $BaSnO_3$ (○), $SrSnO_3$ (△), and $CaSnO_3$ (□) (source was SnO_2 at 293°K).

spectral widths, we took high-temperature x-ray photos of samples of barium and strontium stannate over the temperature ranges 293—893 and 293—843°K, respectively. We used a high temperature x-ray camera of 114 mm diameter. The film was placed asymmetrically, and the periods could be determined to ± 0.001 Å. Figure 5 shows graphs of the variation of the periods with temperature. We see that there are slight anomalies in the region of 650°K for both compounds. In the case of $BaSnO_3$, with increasing temperature there is a small rise in period $\Delta a = 0.004$ Å, while the linear expansion coefficient remains practically the same below and above 650°K: $\alpha_1 = \alpha_2 = 0.9 \times 10^{-5}$ deg^{-1}. In the case of $SrSnO_3$ it is difficult to speak of any noticeable change in period Δa, but there is a definite small change in the slope of the curve above 650°K (below 650°K, $\alpha_1 = 0.8 \times 10^{-5}$ deg^{-1}, while above it, $\alpha_2 = 1.3 \times 10^{-5}$ deg^{-1}).

We may assume that similar structural changes with changing temperature also occur for $CaSnO_3$.

DISCUSSION OF RESULTS

First let us consider the temperature dependence of the factor Z. This dependence cannot be described by a Debye model with the Debye temperature as its single parameter. In fact, for $SrSnO_3$, for example, the effective "Debye temperature" varies from 240°K for T = 78°K to 350°K for T = 1020°K. It would be interesting to compare these values with the Debye temperatures found from data on low temperature specific heats. Unfortunately there are no such data in the literature. If the interatomic forces were the same for all three compounds, then one would expect that $Z(BaSnO_3) < Z(SrSnO_3) < Z(CaSnO_3)$, because of the difference in mass of the atoms of type A, which though not in direct contact with the absorber atoms of type B can still be considered to be their neighbors. The experiment shows (Fig. 3) that this inequality is satisfied for the pairs Ba-Sr and Ba-Ca, while the reverse is true for the pair Sr–Ca: $Z(CaSnO_3) < Z(SrSnO_3)$. This shows the importance of the difference in the interatomic forces for the latter two compounds, which is confirmed by the data on the periods of the unit cells of the crystals. This conclusion is also in agreement with the fact that in calcium stannate the tin ion is "squeezed" tighter than in the other stannates, judging from the geometrical factor t.[8,11]

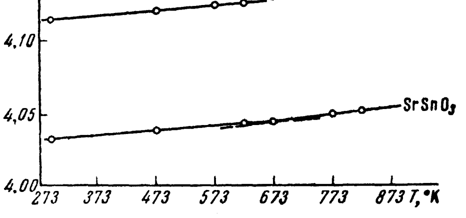

FIG. 5. Temperature dependence of unit cell size for barium and strontium stannate.

Summarizing we may say that in going from Ba to Sr the predominant effect on Z comes from the change in mass of the neighboring atoms, while in going from Sr to Ca the effect of the change in interatomic forces is important. Questions of this kind for diatomic compounds, taking account of interactions with nearest neighbors, are treated quantitatively in the paper of Kagan and Maslov.[12]

The problem of the temperature shift has already been discussed in [1]. At high temperatures the temperature shift for Sn^{119} is given by the relation

$$\Delta E_\gamma \,(\text{mm/sec}) = -3.50 \cdot 10^{-4} \cdot T, \qquad (1)$$

where ΔE_γ is the shift expressed as a velocity. The slope of the straight line portion of the curves $\Delta E_\gamma(T)$ in these crystals is $(3.2 \pm 0.3) \times 10^{-4}$ mm/sec °K, which is slightly less than the computed value (1). The observed value of the shift may be affected by a change in the isomer shift with temperature. In fact one can write the expression

$$E_{\text{abs}} - E_{\text{s}} \sim [R^2_{\text{ex}} - R^2_{\text{gr}}]\,[|\psi(0)|^2_{\text{abs}} - |\psi(0)|^2_{\text{s}}]$$

for the isomer shift, where $E_{abs} - E_s$ is the isomer shift, $|\psi(0)|^2_{abs}$ and $|\psi(0)|^2_s$ are the electron densities at the nucleus in the absorber and source; R_{ex} and R_{gr} are the effective radii of the excited and ground states of the nucleus. From the data given above it follows that with increasing temperature the volume of the unit cell of any of the stannates increases somewhat, so that in principle $|\psi(0)|^2_{abs}$ may decrease.

It has been shown[13] that $R^2_{ex} - R^2_{gr} > 0$ for Sn^{119*}, so that with increasing temperature of the absorber the absolute value of the shift should increase. The fact that the straight line portion of the experimental curves does not exceed the limiting value (1) shows that this effect is small. One might expect that there should be a relative shift of the resonance energy for the different compounds. Such a shift could be caused by a difference in zero-point energy of the lattices and in the densities of electrons at the absorbing nucleus. However, we note that estimates based on data for Z allow one to conclude that the difference in zero-point energy of the lattices does not give a difference in the resonance energies exceeding the experimental error. As for the difference in electron density at the nucleus, because of the decrease in size of the unit cell in going from Ba to Sr and Ca (the electronegativities of these atoms are the same[14]) we should expect an increase in $|\psi(0)|^2_{\text{abs}}$, and consequently, according to (2), a decrease in the absolute value of the shift. The experiment confirms this conclusion for the pairs Ba–Ca and Sr–Ca. From this it follows that the electron density at the Sn nucleus increases considerably when strontium is replaced by calcium. This agrees with the results for the geometrical factor t which were cited earlier. Such an effect is not seen for the pair Ba–Sr.

The observed anomalous change of the periods at T ~ 650°K may possibly be due to a partial reduction of tetravelent tin to divalent with increasing temperature. A similar effect is frequently found for oxides, especially at high temperatures. In our case the reduction obviously already starts at comparatively low temperatures (650°K), in the form of a small but sharp bump at the lowest temperature. Above 650°K the percentage of divalent tin increases with temperature, but this rise now goes continuously. There are two facts which favor our conclusion that there is a transition from tetravalent to divalent tin at 650°K.

First, there are the data on the change in period with temperature. In the case of $BaSnO_3$ there is a small but abrupt increase in the period at 650°K, while for $SrSnO_3$ there is a noticeable change of period with temperature (the linear expansion coefficient is somewhat larger), which may be related to a partial replacement of the small Sn^{4+} ions (0.67 Å) by the large Sn^{2+} ions (1.02 Å).[15]

Second, there are data from electric measurements on solid solutions in the $PbTiO_3$–$SrSnO_3$[16] and $PbTiO_3$–$CaSnO_3$[17] systems.

In both systems, for solid solutions close to $SrSnO_3$ and $CaSnO_3$, the dielectric loss tangent ($\tan\delta$) begins to increase sharply at approximately 650°K. This result can be understood in terms of an increase in conductivity near 650°K, which is actually observed,[17] and which is to be expected from the fact that the appearance of divalent tin ions in the lattice at the positions of tetravalent ions should result in the appearance of "oxygen-like defects" (in order to preserve the neutrality of the lattice).

The results of these experiments which concern the temperature variation of the observed spectral widths give no basis for any categorical statement about the mechanism of this peculiar behavior of the width of the resonance spectrum. But we should like to dwell on certain aspects of this question.

One might think that despite the cubic symmetry of the $BaSnO_3$ cell and the very slight deviation of the cells of $SrSnO_3$ and $CaSnO_3$ from cubic symmetry, the doublet structure of the absorption spectrum existing at $T < 500°K$ must be due to quadrupole interaction, while the decrease in the width of the spectrum in this temperature interval is caused by a decrease in the electric field gradient. But on this assumption it is difficult to reconcile the large change in the splitting (from 0.57 to 0.32 mm/sec in the interval 78—500°K) with the slight change in size of the unit cell. Most probably there is a practically zero field acting on the tin ions, and the field gradients at the positions of these ions are also equal to or close to zero. This conclusion agrees with the conclusions from the structural data. In the cubic cell of $BaSnO_3$, the tin ion is at the center of symmetry, and apparently the tin ions are in similar positions in the cells of $CaSnO_3$ and $SrSnO_3$, since there is justification from the x-ray data[7,8] for regarding the latter as being more or less similar to the cell of perovskite $CaTiO_3$, in which the titanium ion is at a center of symmetry.[18]

The increase in line width with temperature in the range $T > 650°K$ may possibly be related to an anomalous structure change in this region due to partial reduction of tetravalent to divalent tin. It is natural to assume that the temperature broadening of the lines in the stannates and the observed broadening of the lines in SnO_2[1] are of the same kind.

It is not excluded that the mechanism which affects the width and shape of the spectrum is the interaction of the nucleus with the crystalline field induced by the thermal motion of the particles of the crystal. From this point of view the nonmonotonic variation of the width with temperature can be explained on the basis of a definite relation between the nondiagonal and diagonal matrix elements of the dynamic quadrupole interaction. Problems of this kind have been treated theoretically by Bykov.[19] The influence of atomic diffusion in the crystal on the width of the resonance absorption spectrum, which is mentioned by various authors,[20,21] can hardly have a significant effect in our case, since the temperature region investigated is far from the melting point.

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[1] Pham Zuy Hien and V. S. Shpinel', JETP **44**, 393 (1963), Soviet Phys. JETP **17**, 268 (1963).

[2] N. P. Bogorodskiĭ and I. D. Fridberg, Élektrofizicheskie osnovy vysokochastotnoĭ keramiki (Physical Basis of High-frequency Ceramics) GEI, 1958.

[3] Venevtsev, Zhdanov, Solov'ev, and Zubov, Kristallografiya **3**, 473 (1958), Soviet Phys. Crystallography **3**, 471 (1958).

[4] Lyubimov, Venevtsev, Solov'ev, Zhdanov, and Bakushinskiĭ, FTT **4**, 3543 (1962), Soviet Phys. Solid State **4**, 2594 (1963).

[5] Lyubimov, Venevtsev, and Koĭranskaya, Kristallografiya **7**, 6 (1962), Soviet Phys. Crystallography **7**,0 (1962).

[6] R. R. Hewitt, Phys. Rev. **121**, 45 (1961).

[7] J. Smith and A. J. F. Welch, Acta Cryst. **13**, 8, 653 (1960).

[8] H. D. Megaw, Proc. Phys. Soc. (London) **58**, 133 (1946).

[9] G. A. Bykov and Pham Zuy Hien, JETP **43**, 909 (1962), Soviet Phys. JETP **16**, 646 (1963).

[10] Bryukhanov, Delyagin, Opalenko, and Shpinel', JETP **43**, 432 (1962), Soviet Phys. JETP **16**, 310 (1963).

[11] Yu. N. Venevtsev and G. S. Zhdanov, Izv. AN SSSR, ser. fiz. **21**, 275 (1957), Columbia Tech. Transl. p. 277.

[12] Yu. M. Kagan and V. A. Maslov, JETP **41**, 1296 (1961), Soviet Phys. JETP **14**, 922 (1962).

[13] Shpinel', Bryukhanov, and Delyagin, JETP **41**, 1767 (1961), Soviet Phys. JETP **14**, 1256 (1962).

[14] S. S. Bogdanov, Élektrootritsatel'nost' élementov i ikh khimicheskaya svyaz' (Electronegativity of the Elements and Their Chemical Bond) Press of Siberian Section, Academy of Sciences, USSR.

[15] G. B. Bokiĭ, Vvedenie v kristallokhimiyu (Introduction to Crystal Chemistry) Press, Moscow State University, 1954.

[16] Fedulov, Venevtsev, Zhdanov, and Smazhevskaya, FTT **3**, 959 (1961), Soviet Phys. Solid State **3**, 695 (1961-2)

[17] S. A. Fedulov, Dissertation, L. Ya. Karpov Institute, 1962.

[18] H. F. Kay and P. C. Baily, Acta Cryst. **10**, 219 (1957).

[19] G. A. Bykov, JETP **44**, 249 (1963), Soviet Phys. JETP **17**, 171 (1963).

[20] K. S. Singwi and A. Sjölander, Phys. Rev. **120**, 1093 (1960).

[21] Boyle, Bunbury, Edwards, and Hall, Proc. Phys. Soc. (London) **77**, 129 (1961).

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301