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Effect of one-dimensional modes on the Lamb-Mössbauer recoilless factor and second-order Doppler shift of Zn^{2+} in a ZnF_2 crystal in the temperature range 0–55.3 K

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A model for the acoustic-phonon distribution function of Zn^{2+} ions in single-crystal ZnF_2 is suggested that not only explains successfully the recently observed anisotropic mean-square displacements and second-order Doppler shifts in the temperature range 0–55.3 K but also takes into account the chain structure in ZnF_2 formed by distorted F^--ion octahedra, with Zn^{2+} at the center of each octahedron, having different interchain bindings along the crystallographic *c* axis and perpendicular to it. The effect of one-dimensional modes is found to be significant in all the reported studies.

Recently Steiner *et al.*[1] have reported the measured values of the Lamb-Mössbauer recoilless factor (LMF) and the second-order Doppler (SOD) shift in ZnF_2 using the high-resolution 93.3-keV Mössbauer transition of ^{67}Zn in the temperature range 4.2–55.3 K. The measured values of the LMF are markedly anisotropic yielding quite different values of the mean-square displacements (MSD's) of Zn parallel and perpendicular to the main component of the electric field gradient (EFG) tensor. The main component of the EFG tensor is perpendicular to the crystallographic *c* axis. Thus, $\langle x_\perp^2 \rangle$ are MSD's parallel to the *c* axis and $\langle x_\parallel^2 \rangle$ perpendicular to it. From their measurements it is clear that at a given temperature $\langle x_\parallel^2 \rangle$ is larger than the corresponding value of $\langle x_\perp^2 \rangle$. Such an anisotropic behavior of the dynamics of Zn^{2+} can be related to the crystal structure of ZnF_2. Though the unit cell of ZnF_2 is tetragonal with $a=b=4.7034$ Å and $c/a=0.6662$, it can also be visualized as consisting of chains of distorted fluorine-ion octahedra with Zn^{2+} ions occupying the centers of the octahedra, i.e., each Zn^{2+} is surrounded by a distorted octahedron. Further, the chains along the *c* axis are tightly packed in comparison with those perpendicular to it. This is also corroborated through the measured values of the compressibility along the *c* axis and perpendicular to it, which are quite different from each other, the latter being twice that of the former.[2] Thus, unlike another study[1] we suggest that the dynamics of Zn^{2+} is influenced by (i) one-dimensional (1D) modes, i.e., chain modes and (ii) by different degrees of binding of the chains parallel to the *c* axis and perpendicular to it. In what follows, we investigate such a proposition.

The observed temperature-dependent MSD's of a Zn atom, in its hcp crystal, along the c axis and perpendicular to it are also quite different from one another[3,4] but such an anisotropic MSD can be related to the presence of planar modes in a zinc crystal similar to that in a graphite crystal, as has been shown recently by us.[5,6] The motion of Zn^{2+} in ZnF_2, on the other hand, would contain 1D modes quite similar to those present in polymeric crystals like polyethylene, polytetrafluoroethylene, etc.[7–14] We therefore suggest the following phonon frequency distribution function (FDF) for the motion of Zn^{2+} in ZnF_z:

$$g_i(\nu)=\begin{cases} A_i\nu^2\ , & 0\le\nu\le\nu_{0i} \\ B_i\ , & \nu_{0i}\le\nu\le\nu_{mi} \\ 0\ , & \nu>\nu_{mi} \end{cases} \tag{1}$$

where *i* represents the directions parallel and perpendicular to the main component of the EFG tensor, A_i and B_i are constants and can be determined using (i) the continuity of the two distribution functions at ν_{0i} and (ii) the total number of modes along any direction is equal to *N*.

Since we are interested in low-temperature values (0–55.3 K) of the MSD and mean-square velocity, which is related to the SOD shift, we have ignored the dispersion factor in the suggested phonon FDF.

Using Eq. (1), one can obtain the following expressions for the MSD, $\langle x_i^2\rangle$ (Refs. 10, 5, and 6) and SOD, $\delta_{T,i}$ (Ref. 5) in a given direction *i*:

$$\langle x_i^2\rangle=\frac{\hbar^2}{2Mk_B\Theta_{0i}}\left[\delta-\frac{2}{3}\right]^{-1}\left[\left[\frac{1}{2}+\ln\delta\right]+\frac{2}{\epsilon_3^2}\int_0^{\epsilon_3}\frac{x}{(e^x-1)}dx+2\int_{\epsilon_3}^{\epsilon_2}\frac{1}{x(e^x-1)}dx\right], \tag{2}$$

$$\delta_{T,i}=\frac{-3k_BT}{2Mc(3\epsilon_2-2\epsilon_3)}\left[\left[\frac{2\epsilon_2^2-\epsilon_3^2}{8}\right]+\frac{1}{\epsilon_3^2}\int_0^{\epsilon_3}\frac{x^3}{e^x-1}dx+\int_{\epsilon_3}^{\epsilon_2}\frac{x}{(e^x-1)}dx\right], \tag{3}$$

where *M* is the mass of the vibrating unit, k_B is the Boltmann constant, $\delta=\nu_{mi}/\nu_{0i}$, $\Theta_{0i}=h\nu_{0i}/k_B$, $\Theta_{mi}=h\nu_{mi}/k_B$, $\epsilon_3=\Theta_{0i}/T$, and $\epsilon_2=\Theta_{mi}/T$. The total SOD, δ_T, is given by

$$\delta_T = \delta_{T,\parallel} + 2\delta_{T,\perp} \,. \tag{4}$$

It is easy to see that the MSD in a given direction has two components, (i) three dimensional (3D) and (ii) one dimensional (1D). The total recoilless factor in a given direction is therefore the product of 3D and 1D recoilless factors.

Making use of Eq. (2) we have evaluated $\langle x_\parallel^2 \rangle$ and $\langle x_\perp^2 \rangle$ for various sets of Θ_{0i} and Θ_{mi}. We find that the observed $\langle x_\parallel^2 \rangle$ and $\langle x_\perp^2 \rangle$ in the temperature range 4.2–55.3 K (Ref. 1) can be explained reasonably well, as shown in Fig. 1, using the two characteristic temperatures in a given direction ($\Theta_{o\parallel}$ = 100 K, $\Theta_{m\parallel}$ = 350 K) and ($\Theta_{o\perp}$ = 200 K, $\Theta_{m\perp}$ = 350 K), respectively. It may be noted that $\Theta_{o\parallel}$ is almost half of $\Theta_{o\perp}$. Θ_{0i} represents essentially the interchain binding and therefore the chains perpendicular to the c axis are loosely bound in comparison with the binding of the chains in the c-direction in agreement with the observed behavior of ZnF_2.[2] The upper limits of intrachain vibrations remain the same in the parallel and perpendicular directions, i.e., $\Theta_{m\parallel} = \Theta_{m\perp}$ = 350 K.

However, the extent of the presence of linear modes is much larger in $g_\parallel(\nu)$ than in $g_\perp(\nu)$. In Fig. 1 we have also plotted the contributions of 3D and 1D modes for the two MSD's. In both the cases the contribution of 1D modes denoted by curves 1 and 4 for $\langle x_\parallel^2 \rangle$ and $\langle x_\perp^2 \rangle$, respectively, is significant, being larger for $\langle x_\parallel^2 \rangle$. However, the temperature dependence gets reflected essentially in the 3D modes shown by curves 2 and 3 for $\langle x_\parallel^2 \rangle$ and $\langle x_\perp^2 \rangle$, respectively. Thus, we can conclude that in the dynamics of Zn^{2+} in the ZnF_2 crystal, one-dimensional modes play a significant role.

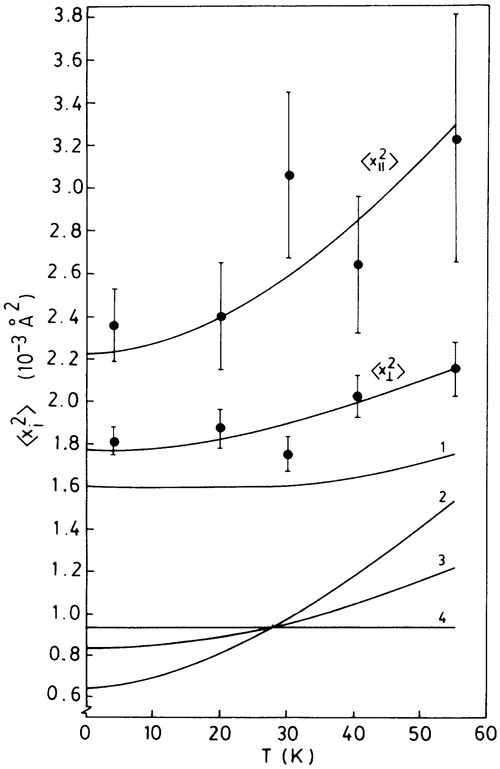

FIG. 1. Comparison of the calculated values of temperature-dependent MSD's of Zn^{2+} in the ZnF_2 polycrystal parallel to the crystallographic c axis, $\langle x_\perp^2 \rangle$, and perpendicular to it, $\langle x_\parallel^2 \rangle$, with the corresponding experimental results (Ref. 1), , in the temperature range 0–55.3 K. Curves 1 and 2 represent, respectively, the one- and three-dimensional contributions to $\langle x_\parallel^2 \rangle$. Curves 4 and 5 represent the same for $\langle x_\perp^2 \rangle$.

We may add that the calculated values of the temperature-dependent anisotropic parameter, $B = k^2(\langle x_\parallel^2 \rangle - \langle x_\perp^2 \rangle)$, where $\hbar|\mathbf{k}|$ is the magnitude of the momentum of the Mössbauer γ radiation, are also in reasonable agreement with the corresponding experimental results.[1] Further, the calculated values of specific heat based on our model for $11 \le T \le 30$ K are in somewhat better agreement with the corresponding experimental results[15] than those given by the isotropic Debye temperature $\Theta_{sp} = 270$ K. However for $T > 30$ K, the specific-heat values given by $\Theta_{sp} = 270$ K are larger than our calculated values, but are quite smaller than the corresponding experimental data[15] as has also been observed earlier.[1]

In Fig. 2(a), we have plotted Δ_{SOD}, which is the temperature-dependent SOD shift relative to its value at 4.2 K along with the experimental results of Steiner *et al.*[1] in the temperature range 4.2–55.3 K. The calculated values have been obtained using expressions (3) and (4) with the same set of characteristic temperatures utilized earlier in MSD studies. As is clear from the figure, the calculated values are in reasonable agreement with the corresponding experimental results in the entire temperature range. In Fig. 2(b) are shown the details of our calculations comprising 3D and 1D contributions at different temperatures to δ_T, i.e., SOD, given by the

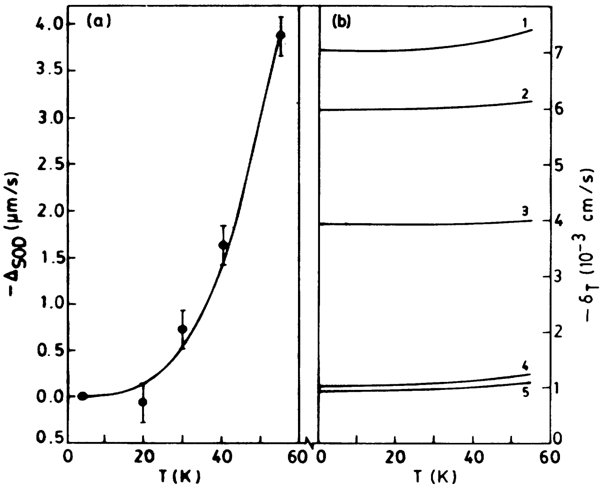

FIG. 2. (a) Comparison of the second-order Doppler shift relative to its value at 4.2 K of Zn^{2+} in the ZnF_2 polycrystal with the corresponding experimental results (Ref. 1), ⫯ , in the temperature range 4.2–55.3 K. (b) Details of the calculations of second-order Doppler shift, δ_T, in the temperature range 0–55.3 K. Curve 1 shows total SOD shift. Curves 2 and 4 represent, respectively, the total one- and three-dimensional contributions to curve 1. Curves 3 and 5 represent, respectively, the total one- and three-dimensional contributions to the SOD shift along the c axis.

center shift of the Mössbauer radiation. While curve 1 represents the total δ_T, curves 2 and 4 represent, respectively, the total contributions of 1D and 3D modes to δ_T, i.e., total 1D and 3D contributions from all directions. The contribution of 1D modes is dominant, being ~ 85% of the total δ_T. In the figure are also shown curves 3 and 5, depicting the total 1D and 3D contributions along the *c* axis. It is therefore obvious that even along the *c* axis and perpendicular to it, the contributions of 1D modes are quite significant.

From our study, we conclude that it is possible to suggest a dynamical model common to both the MSD and SOD shift of a Zn^{2+} ion in the ZnF_2 crystal, which not only goes beyond the Debye and extended Debye model but also successfully explains the recently observed temperature-dependent MSD and SOD shift and is also consistent with the chain structure of the ZnF_2 crystal. In all the studies, the effect of one-dimensional modes turns out to be quite significant.

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