

ON THE MAGNETIC FIELD EFFECT ON THE SOUND VELOCITY OF A DILUTE KRAMERS-ION GLASS AT LOW TEMPERATURE

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Recent results on the magnetic field effect on the sound velocity V in aluminosilicate glasses doped with dysprosium are analyzed on the base of a minimal model for the ground state of Dy^{3+} (Kramers ion with $J = 15/2$) described by a wave function $\varphi_{\pm} = \varphi_{\pm J_m} + \eta\varphi_{\pm 1/2}$. The first term represents the state with a large J projection on a local crystal field axis and the random parameter η ($\langle \eta \rangle = 0, \langle \eta^2 \rangle \ll 1$) introduces a small admixture of the state $\varphi_{\pm 1/2}$ into the ground one. A relative V variation due to resonance interaction of sound waves with this state splitted by H is determined as a function of H and T . It possess an universal asymptotic behavior. Our results are in a reasonable agreement with the experiment. Possible structure of the crystal fields that can induce this state is discussed.

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Introduction. Acoustic wave propagation, phonon echoes, nonlinear magnetic susceptibility and spin echoes of Kramers-ion-doped (Dy, Gd, Eu) aluminosilicate glasses have recently been studied at low T [1,2]. The magnetic field effect on the sound velocity V in Dy doped glasses is one of the typical and important results. Measurements have been performed at $T = 10\text{mK} - 6\text{K}$, $\nu = 100\text{MHz}$ and H up to 50 kG on the samples with ion concentrations $n = 1.5 - 10.1$ at%. Magnetic field was found to modify essentially temperature variation of V . It did not occur in the glass doped with Ho (non-Kramers ion).

Interpretation was based on combining the results of elastic tunneling states (ETS) theory in glasses and the known properties of Kramers ions with a large spin in amorphous material with a random axis of anisotropy ($\mathcal{H} = -DJ_z^2$, where z is direction of the local axis of anisotropy, $J = 15/2$, $D \simeq 120\text{K}$ for Dy^{3+}). The low temperature properties of these glasses in a magnetic field are determined by the magnetic ions whose axis of anisotropy is almost perpendicular to the local field (magnetic TS (MTS)) [3]. Some of these properties are similar to ones of the ETS. However the ETS are characterized by two random parameters (potential asymmetry and tunnel integral) whereas the MTS are described by one parameter (an angle between a local axis and a local field). They may show a similar behavior only when single parameter (energy) is relevant one. A linear T -dependence of specific heat is an example.

In general case there is no such a simple correspondence in behavior of the ETS and the MTS. The relaxation processes were assumed to give $\Delta V \propto \ln(T/T_0)$ for the MTS as it takes place for the ETS. This answer arises as a result of averaging a specific expression, describing interaction of sound waves and the ETS, over two random parameters with a very particular distribution function [4]. Therefore there are no grounds to expect that the MTS relaxation contribution

to ΔV can be presented by product of their density of states and $\ln(T/T_0)$. The second explanation exploits the results of the ETS relaxation by electrons. It requires the existence of the fast MTS. But, as the authors pointed out, the relevant relaxation processes are entirely obscure. Furthermore, this assumption seems to be not confirmed experimentally because minimal spin lattice relaxation time $T_1 \simeq 20\mu\text{s}$ was found for Dy magnetic moments in the glass doped with 0.1at% Dy at $T = 14$ mK [2] whereas the shortest relaxation time $\tau_{\text{min}} < 1\mu\text{s}$ for the ETS in the glass with 1.5at% Dy at the same T [1].

Our purpose is to suggest a new explanation of H influence on V .

Model. Single-ion approximation is used because the effect is proportional to n and exists in a large H (larger than dipolar or exchange interactions). The traditional model mentioned above cannot explain the effect. It leads to extremely weak spin-phonons interaction which depends strongly on H [3]. As a result the resonance processes cannot be responsible for a smooth H dependence of V observed in ref. [1]. The contribution of the relaxation processes to V is the most likely to be suppressed in virtue of inequality $\omega T_1 \gg 1$. Available experimental data don't contradict to this assumption. There are no other data on T_1 for Kramers ions in insulating glasses besides mentioned above. The $T_1 \simeq 10\mu\text{s}$ was found for Ho^{3+} (10at%) in the same glass at 3.5K [5]. Since T_1 of non-Kramers ions ($J = 8$ for Ho^{3+}) is usually shorter than that of Kramers ions both these results allow to assume that for Dy ions $\omega T_1 \gg 1$ at $\nu = 100\text{MHz}$ and $T < 3.5\text{K}$.

Let us consider effects of non-axial electric field gradients. The most general model with a quadrupolar Hamiltonian $\mathcal{H} = \alpha J_x^2 + \beta J_y^2 + \gamma J_z^2$ (α, β and γ are randomly distributed) was found to be nearly equivalent to the simple model ($\mathcal{H} = -DJ_z^2$) when J is large [6]. Therefore, it is unlikely that such a specific Hamiltonian as $\mathcal{H} = -DJ_z^2 - KJ_x^2$ with fixed $D > K$, suggested in [2], realizes for Dy^{3+} ion in the aluminosilicate glasses.

Since in vitreous matrices no clear information on the local crystal field, acting on an rare-earth ion, exists we use a simple minimal model for Dy^{3+} ground state (GS). We shall assume that the GS is described by the wave function $\varphi_{\pm} = \varphi_{\pm J_m} + \eta\varphi_{\pm 1/2}$. The main term $\varphi_{\pm J_m}$ represents the state with a large projection of J ($\pm J_m$) on a direction of a local axis of anisotropy, i.e. ions occupy sites with a predominant axial component in the crystal field. The random parameter η ($\langle \eta \rangle = 0, \langle \eta^2 \rangle \ll 1$) introduces a small admixture of the state $\varphi_{\pm 1/2}$ into the GS. This contribution results from non-axial distortions. Note, the assumption of a slightly and randomly distorted axial symmetry was supported by the spectroscopic data [5]. In a field H removing the degeneracy of the GS the second term is responsible for transitions between two split levels which are produced by the phonons in the first order in the spin-phonon interaction due to change of g -factor on strain. As a result, H effect on V is not suppressed unlike the situation where $\eta = 0$. Such H effect does not occur in the glass doped with non-Kramers ions because electrostatic non-axial distortions lift the degeneracy of the GS which may take place for an axial symmetry.

The terms of the form $\epsilon_n \varphi_{\pm J_n}$ ($3/2 \leq J_n \leq 15/2$, ϵ_n are random parameters), which may occur in the GS, are unessential if $\langle \epsilon_n \rangle = 0$ and $\langle \epsilon_n^2 \rangle \ll 1$ since corresponding splitting $2g\mu J_n \langle \epsilon_n^2 \rangle H \ll 2g\mu J_m H$ for H parallel to the local axis, these terms don't generate a splitting $\propto H$ if H directed perpendicular to the axis and don't influence on a resonant coupling of a sound wave with the GS.

The effect of the ligand fields is described by the Hamiltonian $\mathcal{H} = \sum B_n^m O_n^m$, where O_n^m are spin operators [7]. We assume that an axial part of \mathcal{H} is well definite i.e. the standard deviations of the B_n^0 ($n=2,4,6$) are small in comparison with their mean values. The non-axial coefficients vary considerably and have negligible small mean values. This part of \mathcal{H} is a weak disturbance. These assumptions are consistent with work [8] where crystal fields were investigated numerically for a random dense packing sphere model in single element material. It gives an example of the typical glass local field with the dominant terms of an axial symmetry.

Using the matrix elements of O_n^0 [7], it can be found that the axial part generates the GS with the large J_m ($\geq 11/2$ for definiteness) in a rather wide region of B_n^0 variations.

Let us consider some important examples. The crystal field of the form: $O_4^0 + B_6^0 O_6^0$ leads to the GS with $J_m = 13/2$ when $B_6^0 > 5/3$. The $B_2^0 O_2^0$ term doesn't change it if $0 \geq B_2^0 > -(26/3 + 13/3 B_6^0)$. The small trigonal components $\eta B_6^0 O_6^0$ and $\epsilon_n B_n^3 O_n^3$ ($n=4,6$) (reference to this local symmetry can be found in work [5]) admixture the state $\eta\varphi_{\pm 1/2}$ to the GS and give unessential terms $\epsilon_n \varphi_{\pm 7/2}$. For $J_m = 11/2$ the needed admixture can be generated by a term $O_6^5 \propto \{J_+^5 J_z + J_z J_-^5\}_s$. This typical glass term was found to be the dominant non-axial component in the model [8]. If O_6^0 term is also important the admixture is characterized by two random parameters: $\eta_1 \varphi_{1/2} + \eta_2 \varphi_{-1/2}$. In this case V exhibits more strong T -dependence (see below). Finally, for $J_m = 15/2$ the component $\varphi_{\pm 1/2}$ comes to the GS in the second order of perturbation theory (typically in the form $\eta_1 \eta_2 \varphi_{\pm 1/2}$). For this admixture the $V(T, H)$ is very similar to that of the one parametric case.

In order to use a minimal number of free parameters, the coefficients B_n^m of non-axial distortions were assumed above to be real quantities. It means that a local environment of the ion possesses a plane symmetry containing the local axis.

$V(T, H)$ for the GS eq.(1). The splitting, that depends on the angle ϑ between the local axis and H , is

$$\Delta E(\vartheta, \eta) = 2g\mu H f(\vartheta, \eta), \quad f(\vartheta, \eta) = (p_{\parallel}^2(\eta) \cos^2 \vartheta + p_{\perp}^2(\eta) \sin^2 \vartheta)^{1/2}, \quad (1)$$

$$p_{\parallel}(\eta) = (J_m + 1/2\eta^2)(1 + \eta^2)^{-1}, \quad p_{\perp}(\eta) = (J + 1/2)\eta^2(2(1 + \eta^2))^{-1}. \quad (2)$$

Interaction of a sound wave with the ions due to change of g -factor on strain can be written [9]

$$H' = \frac{1}{2} g\mu \sum_{i,k} t_{ik} (H_i J_k + H_k J_i), \quad t_{ik} = \sum_{l,m} F_{iklm} e_{lm},$$

where \hat{F} is the tensor of spin-phonons coupling, \hat{e} is the strain tensor and $e_{lm} = (V_l V_m / V^2) e_0$ (e_0 is the strain amplitude) for longitudinal waves used in [1]. It is expected that in glasses there are no relations among the components of \hat{F} imposed by the local symmetry and they can be treated as independent of the anisotropy axis orientations random variables [3]. To calculate transitions between the states (1) splitted by H we chose a coordinate system with $H \parallel \hat{z}$ direction in which the transition operator is $t_{xz} J_x + t_{zy} J_y$. For the local axis in (z, x) plane, we have $|\langle \psi_1 | J_x | \psi_2 \rangle| = p_{\parallel} p_{\perp} / f \equiv \omega_{\parallel}$ and $|\langle \psi_1 | J_y | \psi_2 \rangle| = p_{\perp} (\psi_{1,2}$ are wave functions of the states) [7]. Integrating probability transition, obtained

for arbitrary orientation of the axis, over angle φ in (x, y) plane at fixed ϑ yields proportional to $(w_{\parallel}^2 + p_{\perp}^2)(t_{xx}^2 + t_{yy}^2)/2$ expression. Averaging over F_{iklm} distribution leads to an effective dimensionless constant of spin-phonons coupling $\lambda^2 = (t_{xx}^2 + t_{yy}^2)/(2e_0^2)$. It may depend markedly on mutual orientation of H and V.

Using expression for the V variation induced by resonant interaction of a sound wave with two level system at small ω [10] and averaging it over ϑ as well as η distribution, we finally get

$$\delta V(T, H) = \frac{\Delta V}{V} = -\lambda^2 \frac{n}{\rho V^2} \int_0^{\pi/2} \sin \vartheta d\vartheta \int P(\eta) d\eta \frac{M^2(\vartheta, \eta)}{2\Delta E(\vartheta, \eta)} \times \left(1 - 2 \frac{e^{-\beta \Delta E(\vartheta, \eta)}}{1 + e^{-\beta \Delta E(\vartheta, \eta)}} \right), \quad (3)$$

$$M^2(\vartheta, \eta) = (g\mu H)^2 (w_{\parallel}^2(\vartheta, \eta) + p_{\perp}^2(\eta)), \quad w_{\parallel}(\vartheta, \eta) = p_{\parallel}(\eta) p_{\perp}(\eta) (f(\vartheta, \eta))^{-1}, \quad (4)$$

where ρ is the bulk density, $P(\eta)$ is the distribution function. This is δV for the two-level system with the specific form of the splitting and the probability transition M^2 between the levels determined by the two random parameters.

To determine low T -variation of δV for $\Delta E_0/T \gg 1$ ($\Delta E_0 = 2g\mu H J_m$ is the splitting at $\vartheta = \eta = 0$) it is convenient to write $\delta V(T, H) = \delta V_0(H) + \delta \tilde{V}(T, H)$, where $\delta V_0 \propto -H$ is given by the first term of eq.(5) and the second one leads to positive T -dependence of δV .

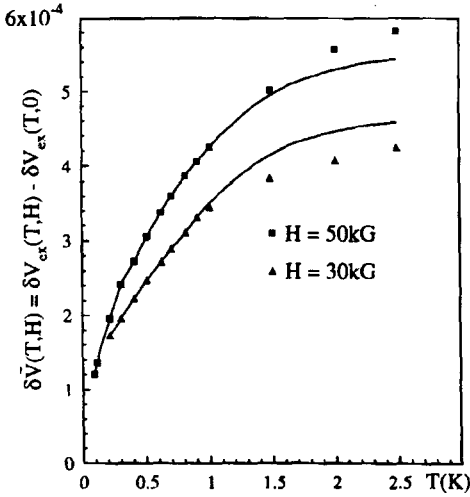
We assume that $\langle \eta^2 \rangle \ll 1$. Hence, one can set $p_{\parallel} \approx J_m$ and $p_{\perp}(\eta) \approx (J + 1/2)\eta^2/2$ (see eq.(3)). Then, in the new variables $\cos \vartheta = r \cos \phi$, $\eta^2 = (2J_m/(J+1/2))r \sin \phi$, we get $\Delta E(r, \phi) = r\Delta E_0 \{1 - ((1/2)r \sin 2\phi)^2\}^{1/2}$. The principal contribution to the integral eq.(5) over r comes from $r \sim T/\Delta E_0$ when $\Delta E_0/T \gg 1$. One can, therefore, keep only the terms of the lowest order in r in the exponential ($\Delta E \approx r\Delta E_0$) and pre-exponential ($M \approx g\mu H w_{\parallel} \approx g\mu H J_m \sin \phi$) factors. Function $P(\eta)$ is assumed to be a single parametrical: $\tilde{P}(\eta/a)a^{-1}$ where a is the scale of η -distribution and $a^2 \ll 1$ corresponds to small uniaxial distortions. Since $\eta/a = (r \sin \phi)^{1/2}/a_0$ ($a_0 = a((J + 1/2)/2J_m)^{1/2}$), there are two regimes of $\delta \tilde{V}$ behavior. If $\Delta E_0 a_0^2/T \gg 1$, one can set $P(\eta) \approx P(0)$ in evaluating integral over r because $(\eta/a)^2 = r \sin \phi/a_0^2 \leq T/\Delta E_0 a_0^2 \ll 1$ for $r \sim T/\Delta E_0$. As a result

$$\delta \tilde{V}(T, H) = C \lambda^2 \frac{n}{\rho V^2} \frac{P(0)}{[(J + 1/2)/2J_m]^{1/2}} (T\Delta E_0)^{1/2}, \quad (5)$$

$$C = \frac{1}{4} \int_0^{\infty} \frac{dx}{x^{1/2}} \frac{e^{-x}}{1 + e^{-x}} \int_0^{\pi/2} (\sin \phi)^{3/2} d\phi \simeq 0.23.$$

Dependence $\Delta \tilde{V} \propto (TH)^{1/2}$ arises from the part of the ions determined by $P(0)$ for which $\Delta E \sim T$. If the low spin component of the GS has the form $\eta_1 \eta_2 \varphi_{\pm 1/2}$ a similar method gives the former result whereas for $\eta_1 \varphi_{1/2} + \eta_2 \varphi_{-1/2}$, one finds $\delta \tilde{V} \propto T$ because the second random parameter introduces the new degree of freedom into the GS.

In regime $\Delta E_0/T \gg 1$ but $\Delta E_0 a_0^2/T \ll 1$ a similar procedure gives $\delta \tilde{V}(H) = \frac{\lambda^2}{8\rho V^2} \Delta E_0$. Here $\delta \tilde{V} \propto H$ is determined by the ions whose ΔE is much less than T and $\delta \tilde{V}$ becomes independent of T . From eqs.(8), (9) one can see that T -dependence of $\delta \tilde{V}$ exhibits crossover at $T \sim \Delta E_0 a_0^2$. In the limiting cases $\delta \tilde{V}$ shows universal behavior which is sensitive to form $P(\eta)$ in the crossover range only.



Relative velocity variation of acoustic waves as a function of T in magnetic fields 30 kG and 50 kG in an aluminosilicate glass containing 10.1 at.% Dy. Points are the experimental data [1]. Solid lines are fit of the results by eqs.(5,7)

Comparison with the experimental data. Since $V(T)$ was measured respectively a reference point $T_0 \approx 30$ mK, T -independent background $\delta V_0(H)$ (7) is assumed to be unessential and $\delta V(T, H) = \delta\tilde{V}(T, H)$ at $T \geq T_0$. The H -effect on V is determined by difference of experimental values $\delta V_{ex}(T, H) - \delta V_{ex}(T, 0) = \delta\tilde{V}(T, H)$. We compare our results with available V -variation in 10 at.% dysprosium doped glass. The simplest step like $P(\eta)$ ($P(\eta) = (1/2)a, -a \leq \eta \leq a$), and $J_m = 13/2$ (for definiteness) are used. As Figure shows T -dependence of $\delta\tilde{V}(T, H)$ at $H = 30$ kG and 50 kG are in a reasonable agreement with the data. The magnitudes of λ and a can be easily obtained because λ^2/a is the only unknown factor of the coefficient in the initial variation of $\delta V \propto T^{1/2}$ ($0.1 \text{ K} \leq T \leq 1 \text{ K}$) and the parameter a determines crossover temperature to $\delta\tilde{V} \propto H$. As a result, using free ion value $g = 4/3$, we find $a \approx 0.3$, $\langle \eta^2 \rangle = (1/3)a^2 \approx 0.03$ and $\lambda \approx 20$. The small $\langle \eta^2 \rangle$ is the essential argument in favor of the model. Rough estimation of λ is $e^2 Z < r^2 > / R^3 \Delta$ [9]; $Z = 3$ is ion charge, r is ion radius, R is ion-ligand distance, Δ is energy of the first exciting level of Dy^{3+} . Using O-Si distance as $R = 1.6 \text{ \AA}$, $\Delta = 3400 \text{ cm}^{-1}$ and $r = 0.95 \text{ \AA}$, we find $\lambda \sim 5$ that is not far from $\lambda \approx 20$.

In the crossover region, the calculated T -variation of $\delta\tilde{V}$ deviates somewhat from the experiment. Since this region is sensitive to changes in $P(\eta)$ agreement can be improved by testing various $P(\eta)$ distributions.

Note, this two level system possesses a wide distribution of one phonons spin lattice relaxation times. At fixed ΔE , T_1 varies from $T_{1 \text{ min}}$ to infinity. In particular, we find $T_{1 \text{ min}} \sim 10 \mu\text{s}$ in $H = 50$ kG for the ions with $\Delta E \approx T \approx 1 \text{ K}$.

In $H \leq 10$ kG, $\delta\tilde{V}(T)$ dependence deviates from the expression for isolated ions that can be attributed to dipolar or exchange interactions between them.

We did not try to explain the change of $V(T)$ behavior in $H = 0$ which occurs when non-magnetic rare-earth La ions are replaced by magnetic ones in this glass. This effect was attributed to the magnetic degrees of freedom [1]. The difference of ionic radii seems to be also or even more important [11]. According to the traditional arguments concerning the structure of glasses, the ions with the equal charges are expected to substitute isostructurally only if they have nearly the same ionic radii. Since La^{3+} ionic radius is 1.216 \AA whereas,

for example, it is 0.95 \AA for Dy^{3+} the glasses doped with these ions may possess different microstructure including essential variations in their ETS parameters and, as result, show different $V(T)$ behavior.

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