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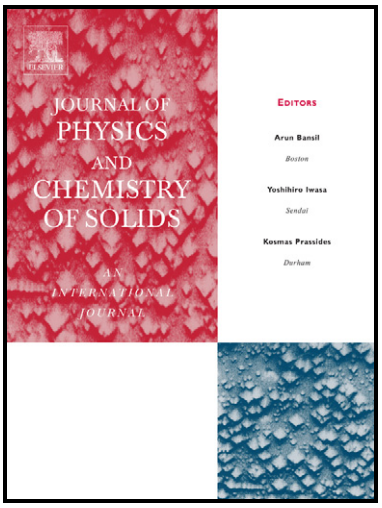

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The ESR study of single crystal spinel $ZnCr_2Se_4$ diluted with Sb and V

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Abstract

The single crystals of Sb^{3+} and V^{3+} doped zinc chromium selenide spinel $ZnCr_2Se_4$ were prepared by a chemical transport method and characterized by ESR spectroscopy in order to examine an effect of nonmagnetic antimony and magnetic vanadium on a properties of the system. For antimony admixtures the Neel temperature is very similar to that of the parent spinel $ZnCr_2Se_4$ (22K). However, upon incorporating vanadium ions, the T_N temperature decreases down to 17.5K, determined for the maximum vanadium content (x=0.06). The temperature dependence of the ESR linewidth over paramagnetic region is interpreted by an occurence of spin-phonon interaction. The strong broadening linewidth together with its strong temperature dependence for vanadium doped $ZnCr_2Se_4$ is explained by the complex paramagnetic relaxation model.

Keywords: single crystals; spinel structure; Electron Spin Resonance; relaxation processes

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1. Introduction

Ternary selenide spinels, exhibiting interesting structural, magnetic and electrical transport properties have been the subject of numerous studies [1-12]. $ZnCr_2Se_4$ is a representative of this class of compounds; it is a cubic normal spinel with Zn^{2+} located at tetrahedral sites (A) and Cr^{3+} occupying octahedral [B] sites of the cubic close-packed array of selenium atoms [1-7]. The physical properties of $ZnCr_2Se_4$ related to the antiferromagnetic behaviour ($T_N = 20$ K) are described in [2-7]. Below T_N the compound reveals complex helimagnetic spin order, which results from competing ferromagnetic and antiferromagnetic interactions. In a number of papers it was shown that the physical properties of spinel systems can be modified by different types and amounts of admixtures located at the tetrahedral and octahedral sites of the spinel structure. The influence of trivalent diamagnetic In, Ga and Al admixtures was reported in Refs. [13-20].

Recently, the structural and magnetic investigations of $ZnCr_2Se_4$ spinel doped with Sb and V ions were carried out [21-23]. The structure refinement was performed using the SHELXL-97 program package showing that all single crystals under study have cubic structure with the space group $Fd\bar{3}m$. The X-ray diffraction results show that the chromium and vanadium ions occupy the octahedral sites and the Sb^{3+} ions share the tetrahedral positions with the Zn^{2+} ions, causing slight increase of the unit cell volume. However, the location of the Sb^{3+} ions in the tetrahedral voids implies some decrease in the total number of the Cr^{3+} ions for the electrostatic charge compensation. In all the samples of (Zn/Sb)-Cr-Se spinels a certain Cr deficit has been observed. Thus, the chemical formula was written as $(Zn_{1-x}Sb_x)[Cr_{2-x/3}]Se_4$.

As expected, the magnetic characteristics of Sb^{3+} substituted system are very similar to those of the parent compound $ZnCr_2Se_4$. The compounds studied are antiferromagnetical with Neel temperature T_N=22K. On increasing Sb-content, some changes in the strength of competing antiferromagnetic and ferromagnetic exchange interactions are likely to occur, which is manifested via the systematic decrease in the magnitudes of the magnetic saturation moment per Cr atom and the paramagnetic Curie temperature. The other magnetic results like the critical metamagnetic fields, the effective magnetic moments and the extent of strong spin fluctuations in the paramagnetic state are nearly the same as in $ZnCr_2Se_4$. Upon incorporating vanadium ions into $ZnCr_2Se_4$, the Neel temperature decreases down to 17.5K, determined for the maximum V content x=0.06. Similarly, the decrease of the paramagnetic Curie temperature up to 38K was observed. It means that the frustration, introduced into the systems by dilution of the B-spinel sublattice with vanadium, reflects the change of ferromagnetic interactions in the magnetic exchange.

The present work is a continuation of studies on the influence of the trivalent ions: antimony and vanadium on the properties $ZnCr_2Se_4$ spinel system. The ESR spectroscopic characterization of the single crystals of $(Zn_{1-x}Sb_x)[Cr_{2-x/3}]Se_4$ and $Zn[Cr_{2-x}V_x]Se_4$ is reported.

2. Experimental

Single crystals of the $ZnCr_2Se_4$ spinel with Sb and V admixtures were grown by the method of chemical vapour transport with anhydrous chromium chloride, $CrCl_3$, as the transporting agent. The details of the synthesis of the $Zn_{1-x}Sb_xCr_2Se_4$ single crystals were described elsewhere [21]. As starting materials for the growth of $ZnCr_{2-x}V_xSe_4$ single crystal, the binary selenide ZnSe, elemental vanadium V and selenium Se (purity > 99.9%) were used. The mixture of the substrates was sealed in quartz ampoules (length ~200mm, inner diameter 20mm) evacuated to ~10^{-3}Pa. These ampoules were heated in a horizontal zone furnace to about 1162K at the solution zone, maintaining a temperature gradient of 60K along the ampoule. The furnace was slowly cooled to room temperature after 10 days of heating. The obtained single crystals had a regular octahedral shape and well-formed regular (111) faces with edge lengths of ~1 to 3 mm.

Chemical composition of single crystals was determined by energy-dispersive X-ray fluorescence spectrometry (EDXRF). The sample was excited by the Rh target X-ray tube of 125μm thickness Be window (XTF 5011/75, Oxford Instruments, USA). The X-ray spectrum from the sample was collected by thermoelectrically cooled Si-PIN detector (XR-100CR Amptek, Bedford, MA, USA), having a resolution of 145 eV at 5.9 keV. The Si-PIN detector was coupled to the multichannel analyzer (PX4 Amptek, Bedford, MA, USA). The position of the sample was obtained using the X-Y stage and monitored by CCD camera and two laser pointers. The applied EDXRF spectrometer is described in details in Ref.[24]. The quantitative analysis of single crystal was performed by fundamental parameters method. The results of EDXRF analysis together with determined chemical formulae are shown in Table 1.

The electron spin resonance spectra were recorded with a standard ESR spectrometer operating at X-band (~9GHz) frequency using 100 kHz field modulation. The microwave frequency was measured using Hewlett Packard 534 microwave frequency counter. The measurements were performed in the temperature range 3-400 K with an Oxford Instruments ESR 910 helium flow cryostat. The ESR spectra were recorded as the derivative dP/dB at different temperatures. The values of ESR parameters, i.e. linewidth (ΔB) and resonance field (B_r), were obtained from the best fit of the simulated Lorentzian profile to the experimentally observed spectra. Figure 1(a,b) shows the experimental and simulated ESR spectra at selected recording temperatures. In both cases, for $ZnCr_2Se_4$ doped with antimony or vanadium, the nominal Sb and V content taken for the chemical syntheses was similar. The actual dopant concentration, derived for selected crystals from the EDXRF method, indicates differences in the amount of dopant. In our study a small, as-grown single crystals with the shape of octahedron without orientation of samples were measured.

3. Results and discussion

3.1. The relaxation processes within paramagnetic region studied by ESR method.

3.1.1. $(Zn_{1-x}Sb_x)[Cr_{2-x/3}]Se_4$

Within the paramagnetic (PM) region, the ESR spectra of both crystals studied showed a single Lorentzian line with g = 1.99 which is attributed to Cr^{3+} ions. The g-values remain constant in the PM temperature range (Fig.2b). In contrast, the ESR linewidth (ΔB) shows behaviors which are dependent on the temperature and independent of the concentration of the chromium ions. The plots of the temperature dependence of the ESR linewidth for: $(Zn_{0.98}Sb_{0.01})[Cr_{1.98}]Se_4$ and $(Zn_{0.97}Sb_{0.02})[Cr_{1.99}]Se_4$ are shown in Fig.2(a). Starting from the T = 400 K, the linewidth decreased as the temperature was reduced to T = 125 K. The ESR linewidth is related to the relaxation of the spin system. For individual spins $\Delta B \sim 1/\tau$, where τ is the spin relaxation time. In a dense magnetic material, this relationship is modified since the magnetization relaxes towards an effective field instead of the external field. The temperature dependence of the ESR linewidth for concentrated magnetic systems at $T >> T_{crit}$ has been discussed in several papers by Seehra et al [e.g.25]. From these studies follows that the temperature dependence of the linewidths outside the critical regions associated with the magnetic transitions, arises from two mechanisms: (i) the phonon modulation of the antisymmetric (Dzialozhinsky-Moriya) exchange interaction - this behavior was found in $[Cu(HCOO)_2*4H_2O]$, [26], and on $CuGeO_3$ [27]; (ii) the phonon modulation of the crystalline field - this behavior was observed for non S-state systems with S≥1, for example $CrBr_3$ [28] and $NiCl_2$ [29]. For $ZnCr_2Se_4$ and $(Zn/Sb)Cr_2Se_4$ spinels the problem of the temperature dependence of the linewidth in the paramagnetic region is similar to that in $CrBr_3$ [28], with S=3/2 for Cr^{3+}. The linear temperature dependence of the ESR linewidth is observed well above $T_N \cong 20K$. From Huber and Seehra theory [28] follows that the linewidth in $ZnCr_2Se_4$ parent spinel and $(Zn/Sb)Cr_2Se_4$ doped spinels ($T>>T_N$) can be described as:

$$\Delta B = \Delta B_{ss} + \Delta B_{s\text{-}ph} \quad (1)$$

where ΔB_{ss} is described by the exchange narrowing theory [30]:

$$\Delta B_{ss} = [(\Delta B_{dd})^2] / B_{ex} \quad (2)$$

(i.e. is proportional to the square of the dipolar produced linewidth ΔB_{dd} divided by the rate of exchange) and $\Delta B_{s\text{-}ph}$ represents the contribution of the spin-phonon interaction.

In ref.[28, eq.A5] a general expression for $\Delta B_{s\text{-}ph}$ is derived. From this it is apparent that a broad band of phonons takes part in the relaxation process. This is in contrast to one phonon relaxation process of a magnetic ion which is isolated from magnetic interactions. In this case, only narrow bands of phonons with energies comparable to the ionic level splitting are involved in one phonon processes. Whereas in the concentrated system, one phonon relaxation is far more effective than it is for an isolated ion. In the latter, except at low temperatures, spin-lattice relaxation is dominated by multi-phonon processes.

3.1.2. The broadening of ESR linewidth in $Zn[Cr_{2-x}V_x]Se_4$

The plots of the temperature dependence of the linewidth, resonance field and spectrum intensity for $Zn_{1.06}[Cr_{1.96}V_{0.04}]Se_4$ and $Zn_{1.04}[Cr_{1.94}V_{0.06}]Se_4$ are shown in Fig.3 (a), (b) and (c), respectively. The resonance spectra consist of the single Lorentzian-shape line. The presence of V^{3+} ions in the $ZnCr_2Se_4$

parent spinel produces a marked broadening of the resonance linewidth in the paramagnetic phase. For $Zn_{1.06}[Cr_{1.96}V_{0.04}]Se_4$ and $Zn_{1.04}[Cr_{1.94}V_{0.06}]Se_4$ ΔB = 139 mT at T = 370K, whereas for $ZnCr_2Se_4$ ΔB = 42.8 mT at the same temperature (see Fig.4). Starting from the T = 400K, the linewidth values decreased as the temperature was reduced to T = 80K. Deviation from linearity is observed. At temperatures above 200K the signal became weak and very broad which made accurate fitting of ESR data difficult (error about 20%). Because of that, a monotonous shift of the resonance field is seen in the paramagnetic region. The value of the parameter $b = \Delta B/\Delta T$ of the thermal broadening linewidth found for both examined compounds is b_{av} = 0.36 mT/K and is significantly higher in comparison with b = 0.11 mT/K for the parent spinel. To understand the origin of the observed linewidth and its temperature dependence we have to compare the relaxation properties of the Cr^{3+} and V^{3+} ions. In the chromium spinels, the Cr^{3+} ions always occupy the B-site of the spinel structure. The local symmetry on this octahedral site leads to a nondegenerate orbital ground state with S=3/2. On the other hand, for the $3d^2$ configuration of V^{3+} (S=1), the ^3F free ion ground state is split by an octahedral field leaving an orbital triplet (T_2) lowest. Because of that, Cr^{3+} is the ion weakly coupled to the lattice in comparison with the fast-relaxing V^{3+} ions [31]. The problem of ESR linewidth for dilute paramagnetic admixtures in an exchange-coupled paramagnetic host has been investigated by Gulley and Jaccarino [32] using the phenomenological coupled equations of motion method. A detailed explanation of these equations and their solutions can be found in their review. The systems investigated contain three distinct components: (1) the host $ZnCr_2Se_4$ subsystem contains Cr^{3+} ions, (2) the admixture subsystem contains V^{3+} ions and (L) the lattice. Figure 5 shows the schematic picture for such a system with arrows indicating possible relaxation paths between the components. The parameters δ_{nm} (n,m = 1,2) are the spin-spin relaxation rate, resulting from the exchange interaction between subsystems; δ_{1L} and δ_{2L} describe the spin-lattice relaxation rate of chromium and vanadium ions, respectively. From the analysis in [32] the ESR linewidth can be written as follows:

$$\Delta B = \Delta B_0 + \{(\chi_V/\chi_{Cr})\, \delta_{21}\, k^2\, [X/(1+X)]\} \qquad (3)$$

where: ΔB_0 is the ESR linewidth of $ZnCr_2Se_4$ spinel; χ_V and χ_{Cr} are magnetic susceptibility of Zn-[Cr/V]-Se and parent spinel, respectively; $k = g_{Cr} / g_V$ and $X = \delta_{2L}/\delta_{21}$ is the bottleneck parameter.

As the parameter X increases, the bottleneck opens, the lines broaden in proportion to δ_{2L} and relaxation of the system is dominated by the fast spin-lattice relaxation rate of the admixture ions. In Zn-(Cr/V)-Se investigated spinels, the introduction of a third element (V^{3+} ions) provides an additional relaxation path created by phonon modulation of the crystalline field. The linewidth behavior results from the variation of the spin-lattice relaxation rate of the vanadium ions. In terms of the parameters of the equation of motion model (eq. 3), the strong increase of linewidth with temperature (b = 0.36mT/K) is consistent with aprogression from a region where δ_{2L} is slow enough (relative to δ_{21}), rendering a system which is more or less bottlenecked. For the region where $\delta_{21} \cong \delta_{21}$ a pronounced broadening is observed.

The system investigated contains two types of magnetic ions: Cr^{3+} and V^{3+}, the former is weakly coupled to the lattice in comparison with the latter. We believe that strong broadening and temperature dependence of linewidth in PM region can be described by the complex paramagnetic relaxation model. The subsystem exchange-coupled Cr^{3+} ions is coupled with lattice: (1) directly (δ_{1L} parameter and ΔB_0 in eq.(3)) and (2) through the admixture subsystem containing V^{3+} ions. The relaxation process (1) is described with Huber-Seehra theory [28] and relaxation (2) by Gulley-Jaccarino theory [32].

3.2. The critical behavior of the electron spin resonance in $(Zn_{1-x}Sb_x)[Cr_{2-x/3}]Se_4$ and $Zn[Cr_{2-x}V_x]Se_4$ spinels

The magnetic investigations of $ZnCr_2Se_4$ spinel doped with Sb and V ions were carried out by some of us [21-23]. According to [23] the magnetic characteristics of Sb^{3+} substituted system are very similar to those of the parent compound $ZnCr_2Se_4$ and the Neel temperature T_N = 22K. Upon incorporating vanadium ions into $ZnCr_2Se_4$, the Neel temperature decreases to 17.5K determined for the maximum V content. In Fig.3(d) the magnetic susceptibility vs temperature data (from [23]) are shown.

The changes of ESR parameters (linewidth ΔB, resonance field B_r and intensity DI obtained from the second integration of field derivative absorption curve – DI values were reduced to T_{max}) in the whole temperature range are illustrated in Figs.2 and 3. As a function of T, the ESR linewidth for all samples decreases to a shallow minimum at 60-65 K, which is above the ordering temperature. With further temperature reduction, the broadening of ΔB is observed; below $T_0 \approx 40$ K , ΔB increases rapidly. This behavior is accompanied by shift of the resonance field as compared to the high-temperature value. At the same time, the spin susceptibility (DI) rapidly increases and exhibits a broad maximum at T_0, well above the ordering temperature determined from magnetic susceptibility experiments [21,23]. At the temperature range from 40 K to 20 K the linewidth increase produces a rapid diminution in the intensity and the spectrum is not longer observed below 17 – 20 K. The observed behavior of the linewidth and resonance field is attributed to critical phenomena while approaching the antiferromagnetic order. The theory of the critical-point anomalies in the ESR linewidth in antiferromagnets was presented by Huber et al [33,34] who demonstrated that the growth of ΔB as $T \rightarrow T_N$ from the high-temperature side reflects the increase in the lifetime and the correlation length of the critical fluctuations. According to the prediction of this theory, anisotropy plays a fundamental role in the nature of the anomaly observed near the Neel temperature. The ESR linewidth near T_N can be written as follows:

$$\Delta B \sim \Delta B_{ncrit}(T) + \Delta B_{crit}(T) \qquad (4)$$

where the factors $\Delta B_{ncrit}(T)$ and $\Delta B_{crit}(T)$ represent the non-critical and critical contributions to the linewidth, respectively. $\Delta B_{ncrit}(T)$ is also a function of temperature, see equations (1) and (3).

The angular dependence of the contributions to the linewidth is interesting. However, the local symmetry of the ligands surrounding the magnetic ion is predominantly cubic in $ZnCr_2Se_4$ and $ZnCr_2Se_4$ - doped spinels and the neighboring selenium ions form a nearly perfect octahedron. In this case, anisotropies in the linewidth are not expected. As is evident in Figs 2a and 3a, the temperature dependence of ESR linewidth in the critical region can be fitted to the empirical relation: $\Delta B \sim (T - T_N)^{\gamma}$ with $\gamma = -0.7$. The same result was obtained in $NiCl_2$ by Birgeneau et al [29].

The shift of the resonance field implies the formation of internal fields. The onset of the resonance field shift at about T=60K means that short range ordering of spins starts to develop from the temperature much higher than T_N. Particularly interesting is the temperature dependence of spin susceptibility. The magnetic structure of $ZnCr_2Se_4$ is characterized by ferromagnetic planes with a turn angle of the spin direction of 42^0 between neighboring planes [3-6]. It is known that below T_N the intensity of the resonance line is expected to decrease as a consequence of the development of a field-dependent energy gap in the frequency-field diagram. The temperature dependence of DI suggested that the magnetic ordering of $ZnCr_2Se_4$ doped by antimony or vanadium ions occurs in a two-step process: during cooling, first, up to T_0, a two-dimensional short-range ferromagnetic correlations grow in the planes of the crystals, then, at T_N, the antiferromagnetic ordering between the planes appears.

4. Conclusions

The following conclusions can be drawn on ESR in $(Zn_{1-x}Sb_x)[Cr_{2-x/3}]Se_4$ and $Zn[Cr_{2-x}V_x]Se_4$ spinels from the results of the experiments performed:

- For $ZnCr_2Se_4$ diluted with antimony, the magnetic characteristic like the ordering temperatures are nearly the same as in parent spinel. Upon incorporating vanadium ions, the Neel temperature decreases down to 17.5K, determined for the maximum V-content x=0.06. The ESR results appear to be in reasonable agreement with the magnetic susceptibility ones.
- The linear temperature dependence of ESR linewidth which is observed for Sb^{3+}-doped $ZnCr_2Se_4$ shows that one-phonon relaxation may prevail in PM materials even at high temperatures. This effect is caused by a broad band of phonons that may participate in the spin relaxation process, in accordance to Huber-Seehra theory [28].
- The strong broadening and strong temperature dependence of linewidth are observed in PM region for V^{3+}-doped $ZnCr_2Se_4$, in comparison with ΔB for parent spinel. These effects are explained by the complex paramagnetic relaxation model.
- The ESR data in critical temperature region suggested that the magnetic ordering of $ZnCr_2Se_4$ doped by antimony or vanadium ions occurs in a two-step process.

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Captions of Figures

Fig.1 (color online). The experimental (dash) and simulated (solid) ESR spectra of $ZnCr_2Se_4$ doped: (a) antimony; (b) vanadium

Fig.2 (color online). The ESR parameters: (a) linewidth; (b) resonance field; (c) relative spin susceptibility calculated as double integration of the spectrum, as a function of the temperature for: $(Zn_{0.98}Sb_{0.01})[Cr_{1.98}]Se_4$ (denoted as-circles) and $(Zn_{0.97}Sb_{0.02})[Cr_{1.99}]Se_4$ (denoted as-triangles); inset shows the relative DI^{-1} vs temperature.

Fig.3 (color online). The ESR parameters: (a) linewidth; (b) resonance field; (c) relative spin susceptibility calculated as double integration of the spectrum, as a function of the temperature (inset shows the relative DI^{-1} vs temperature); (d) dc mass susceptibility vs temperature [...] (inset shows inverse susceptibility) for: $Zn_{1.06}[Cr_{1.96}V_{0.04}]Se_4$ (denoted as-circles) and $Zn_{1.04}[Cr_{1.94}V_{0.06}]Se_4$ (denoted as-triangles);

Fig.4 (color online). The comparison of ESR linewidth as a function of temperature within the paramagnetic region for: (i) $ZnCr_2Se_4$ (denoted as-circles); (ii) $(Zn_{0.98}Sb_{0.01})[Cr_{1.98}]Se_4$ (denoted as-triangles; (iii) $Zn_{1.04}[Cr_{1.94}V_{0.06}]Se_4$ (denoted as-squares).

Fig.5 Model of paramagnetic relaxation processes of the $Zn[Cr_{2-x}V_x]Se_4$ spinel systems.

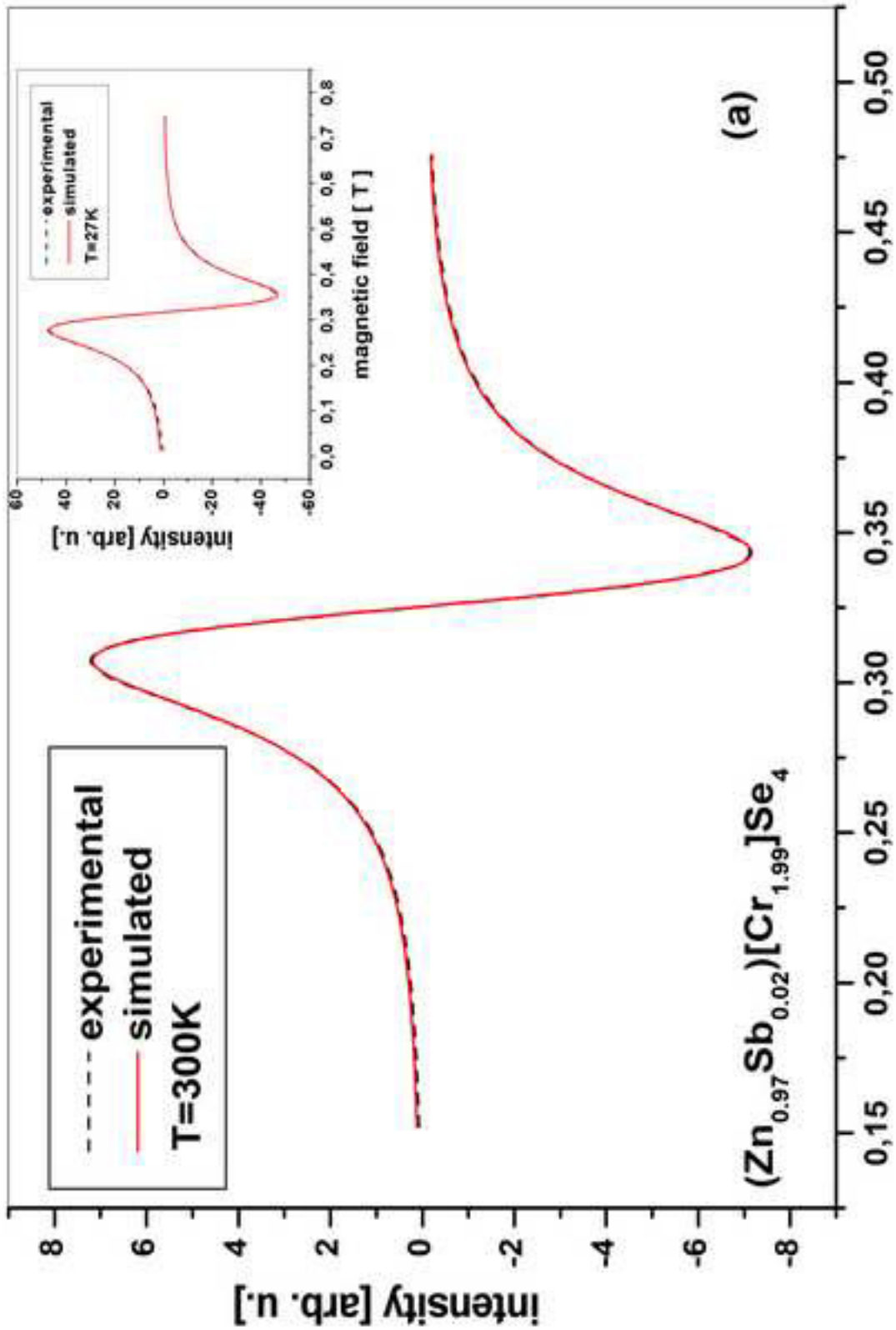

Fig.1

Figure(s)

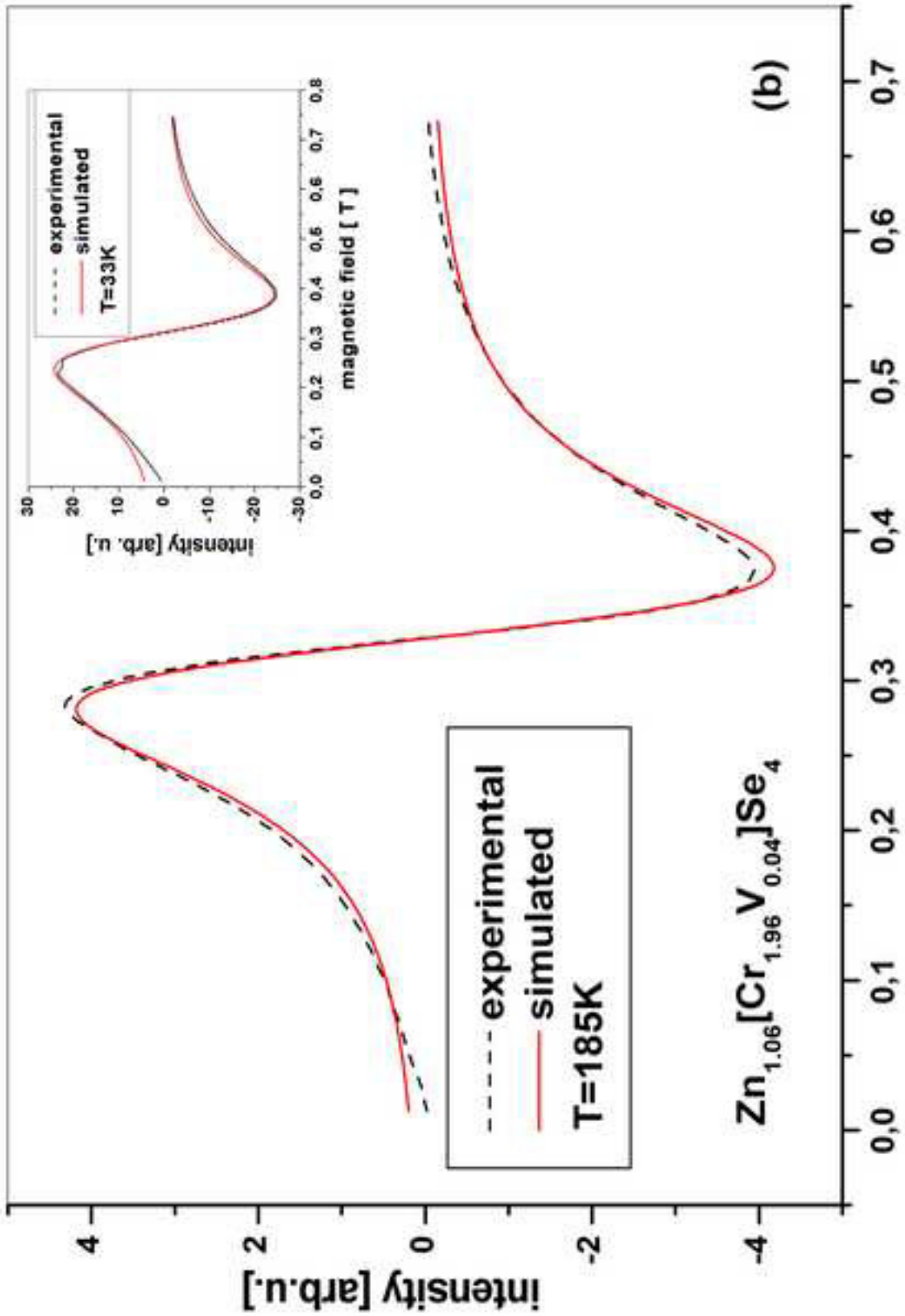

Fig.1

Figure(s)

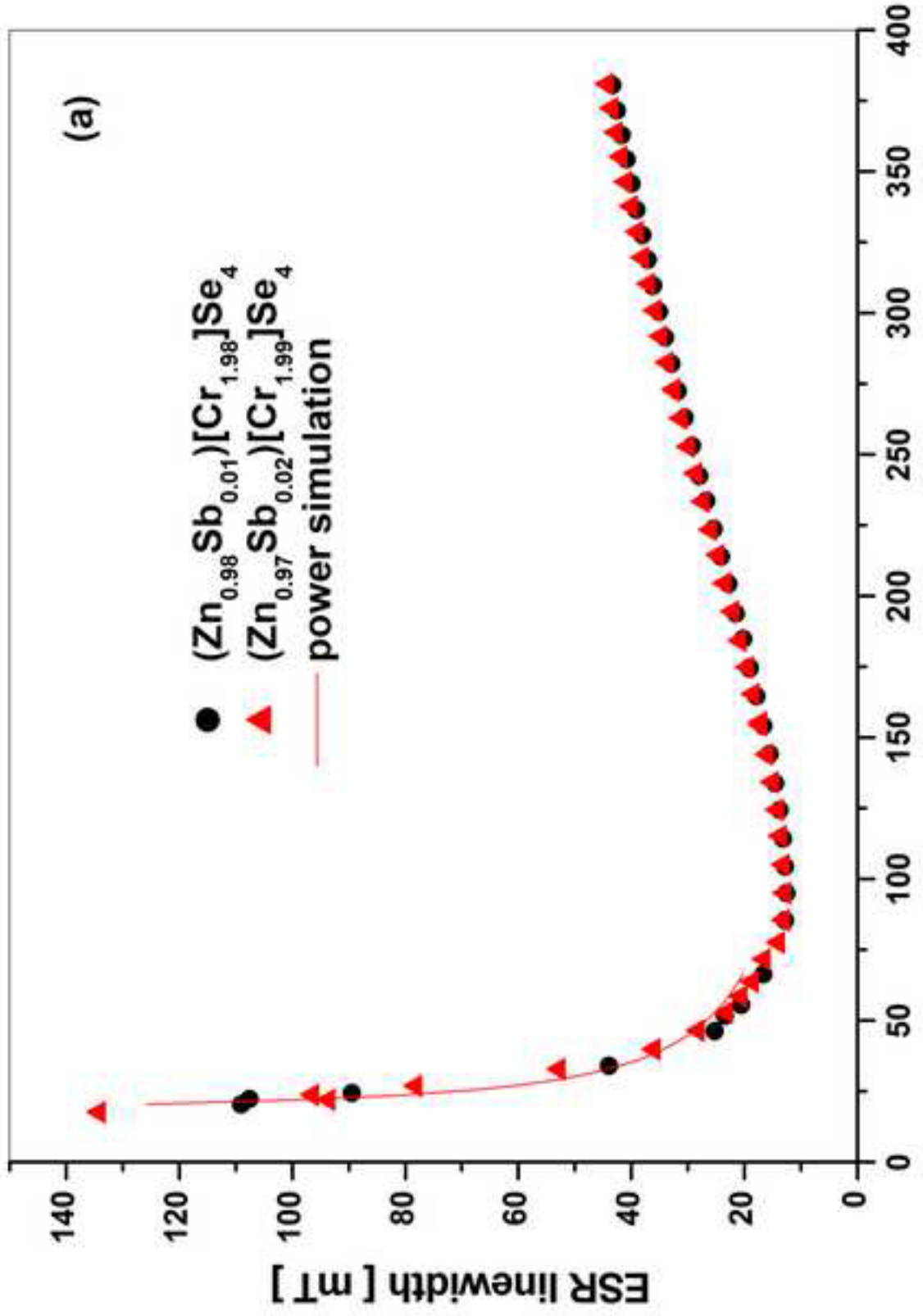

Fig.2

Figure(s)

Figure(s)

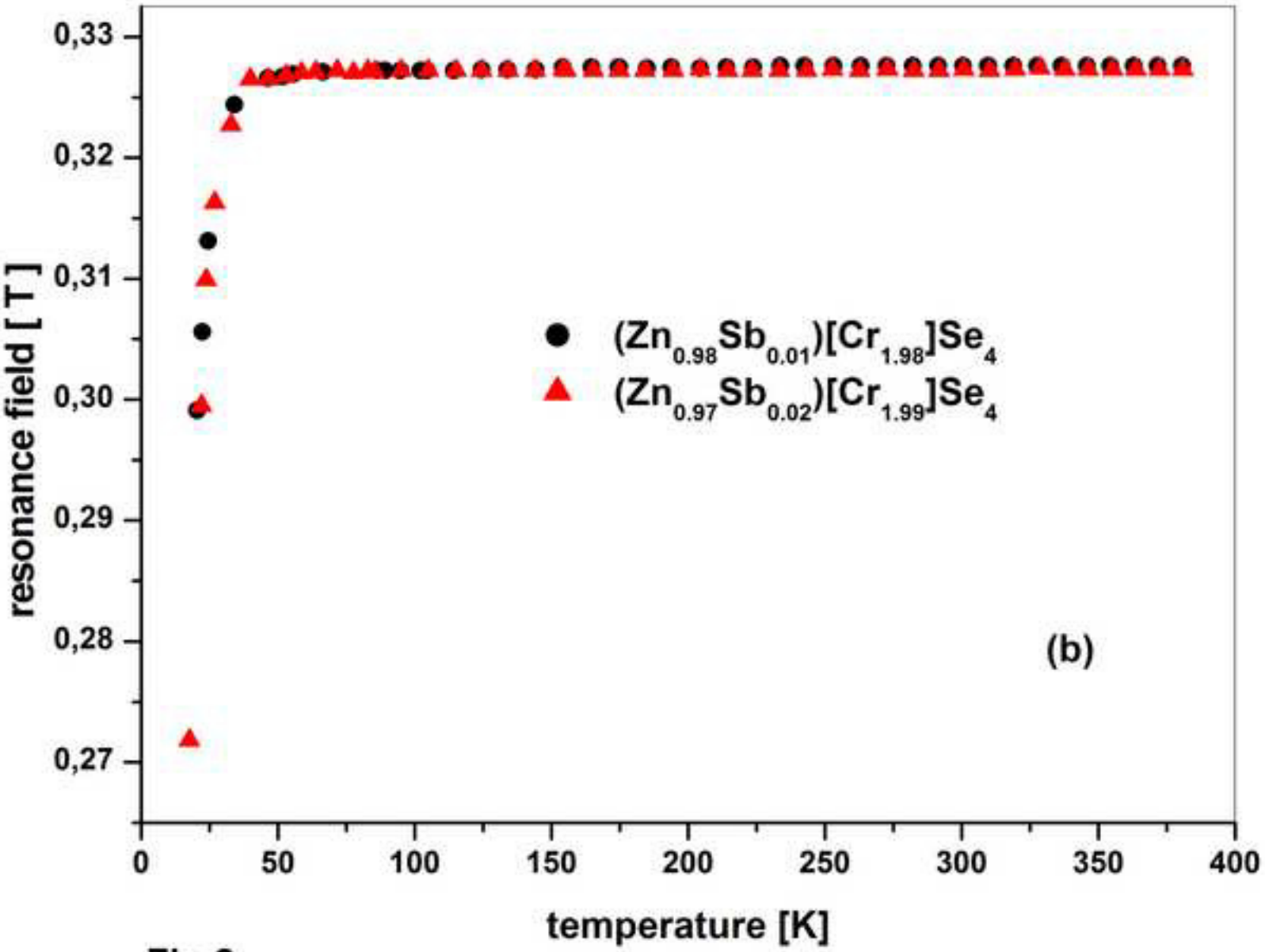

Fig.2

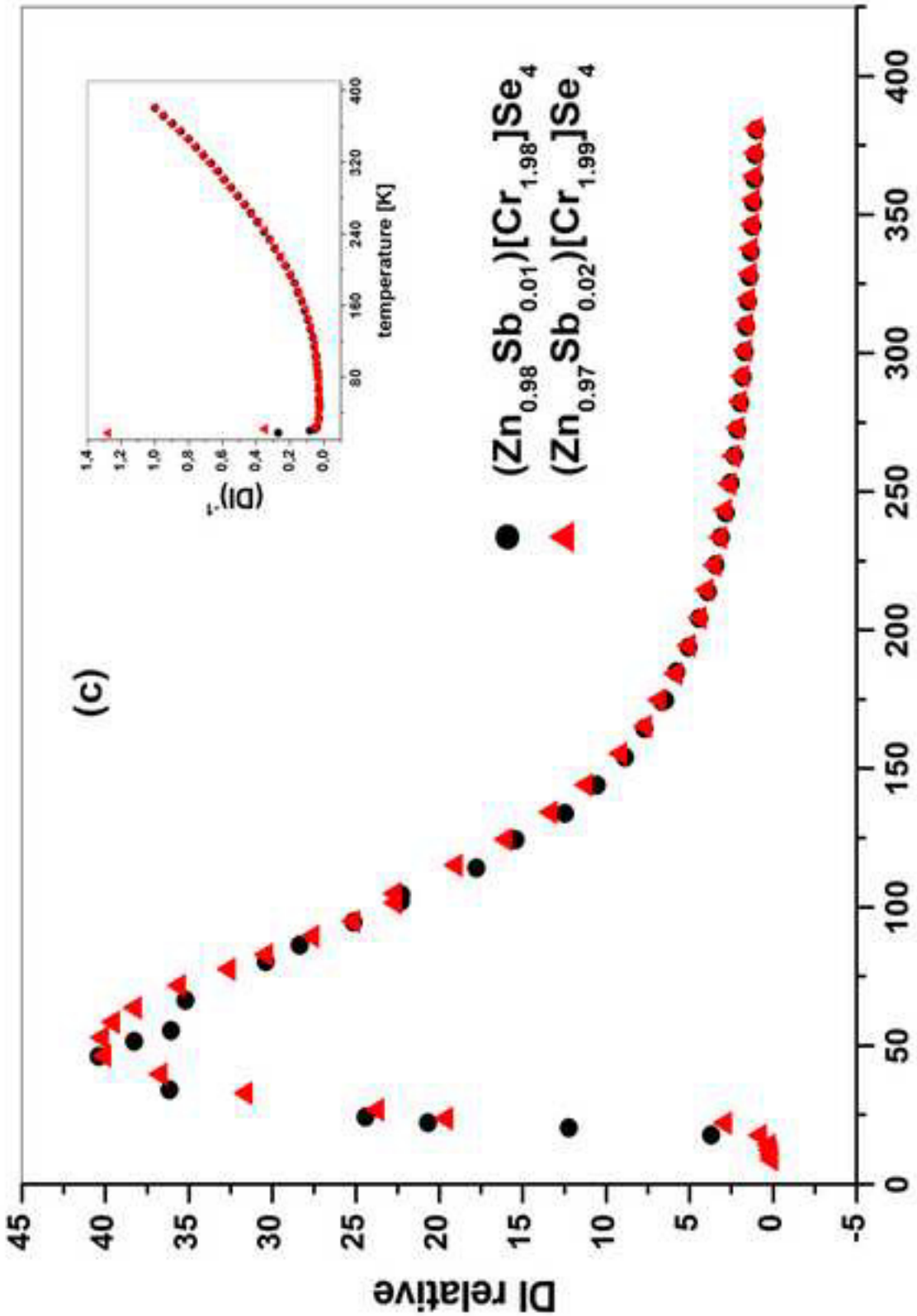

Fig.2

Figure(s)

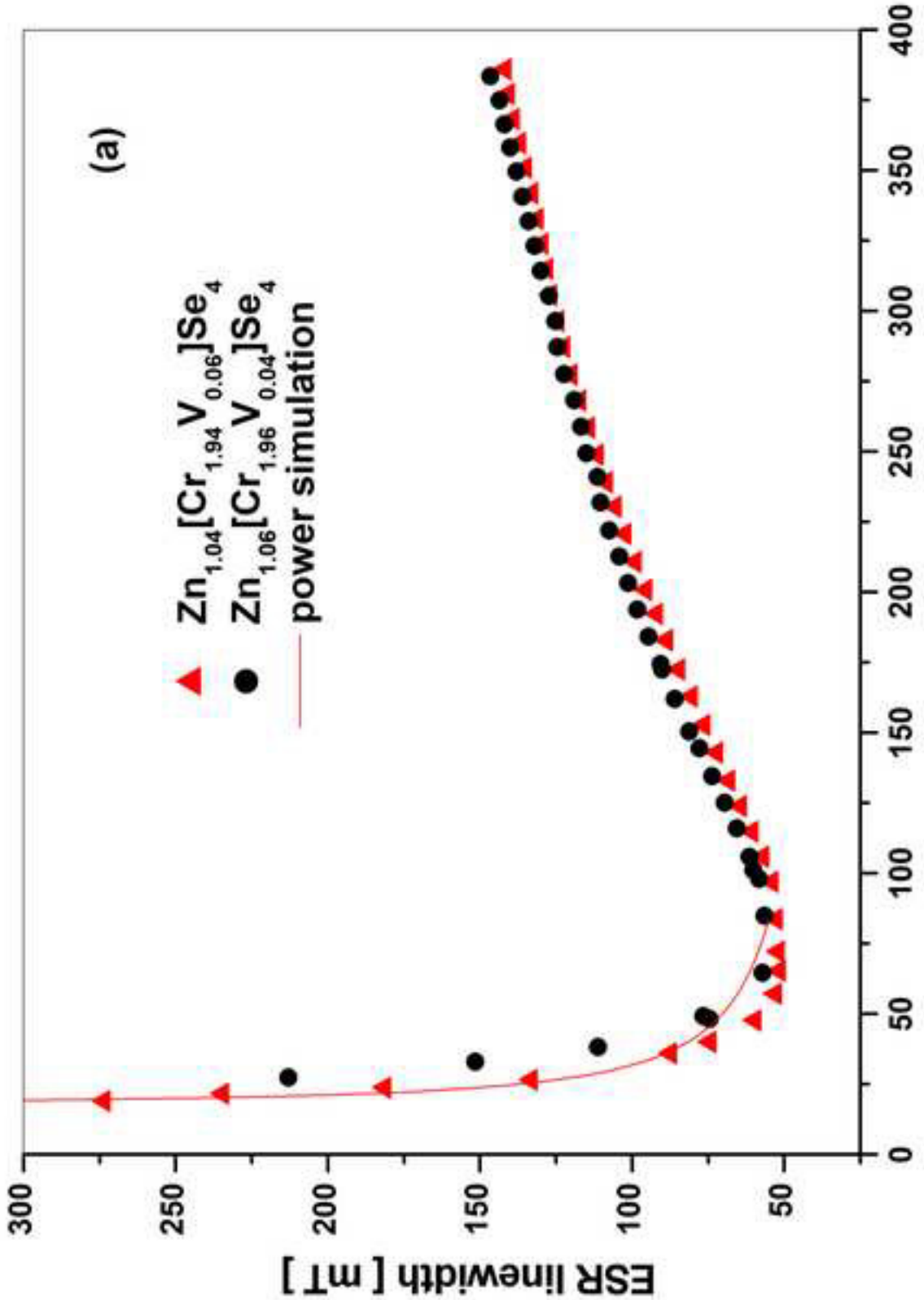

Fig.3

Figure(s)

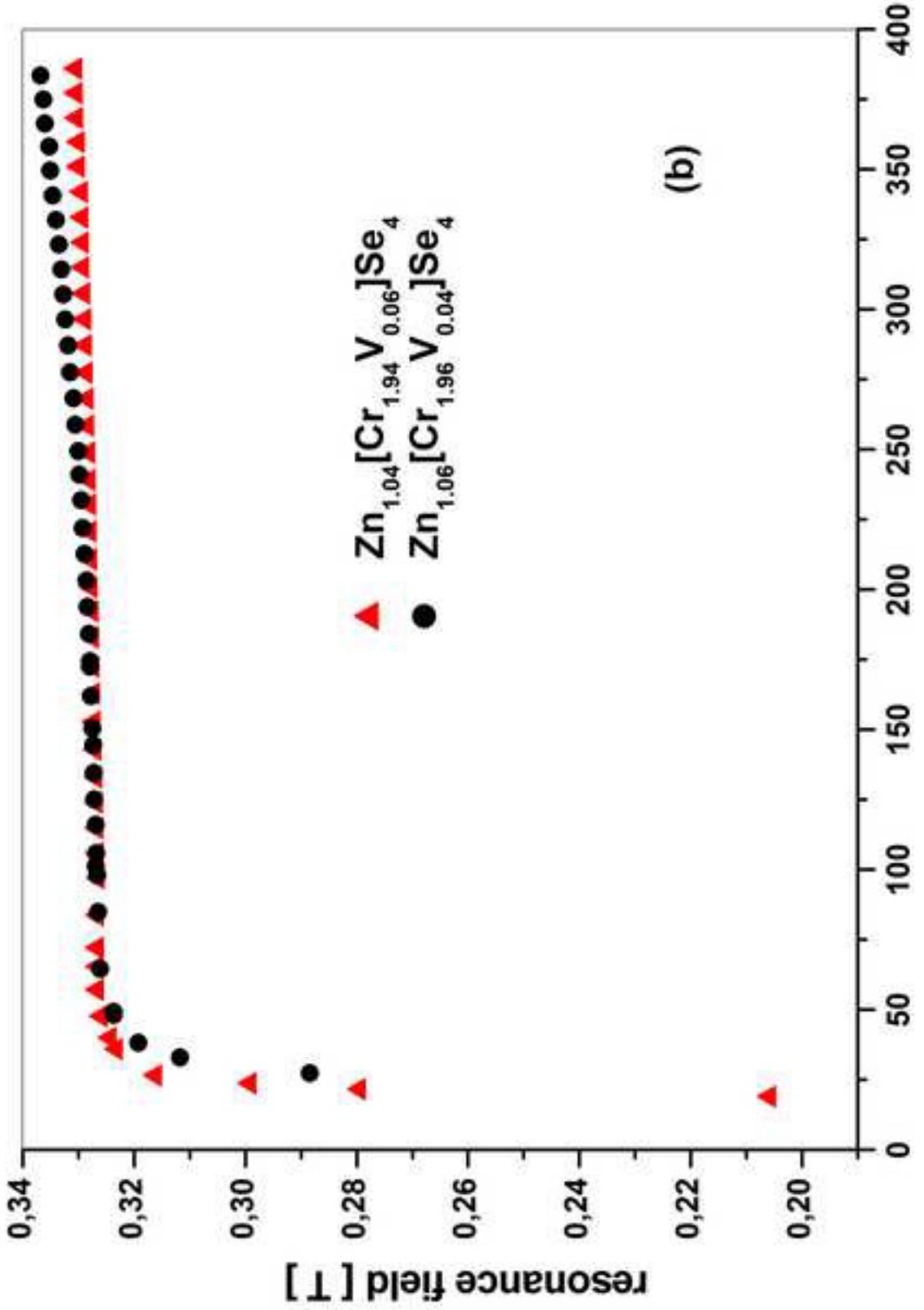

Fig.3

Figure(s)

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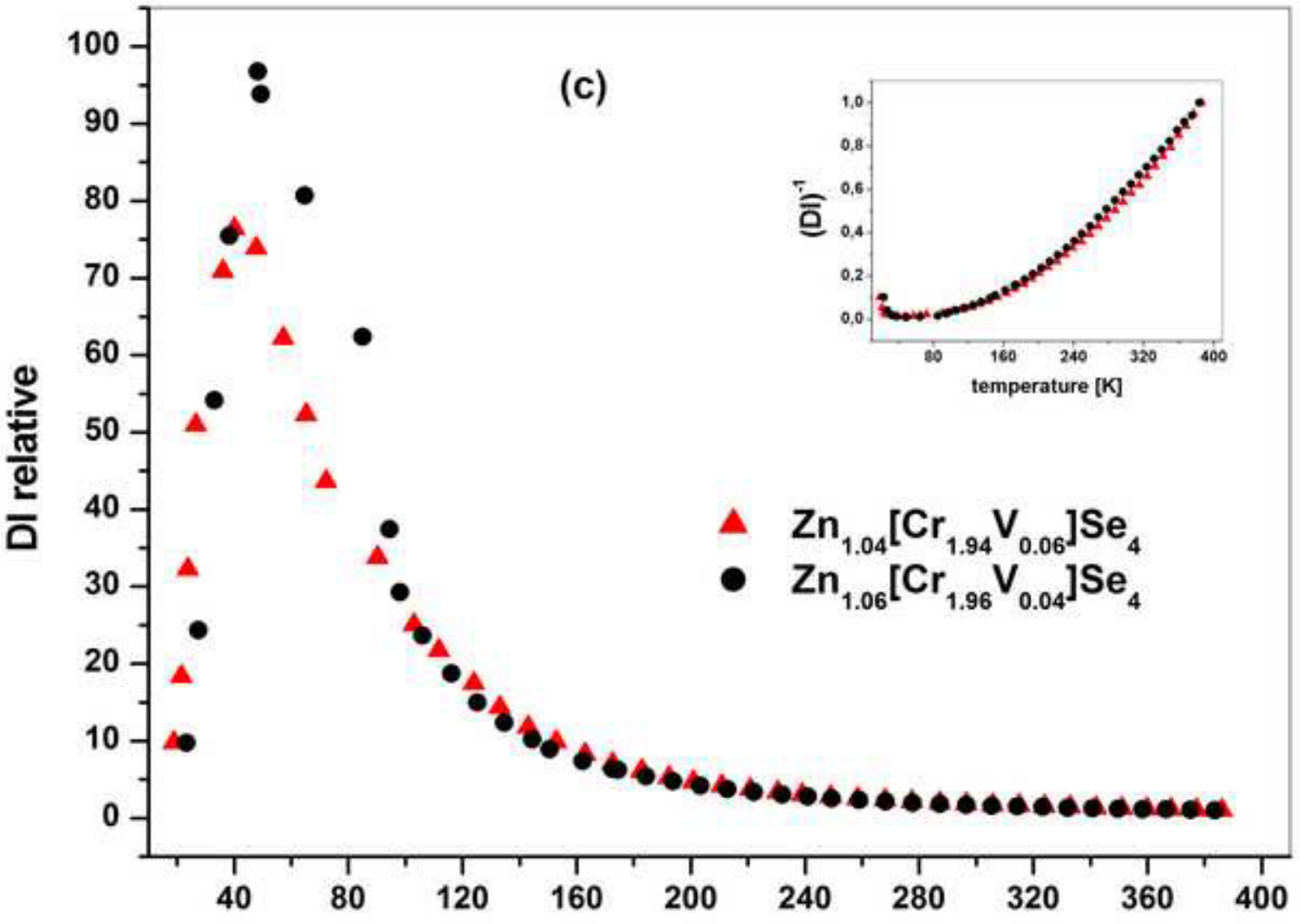
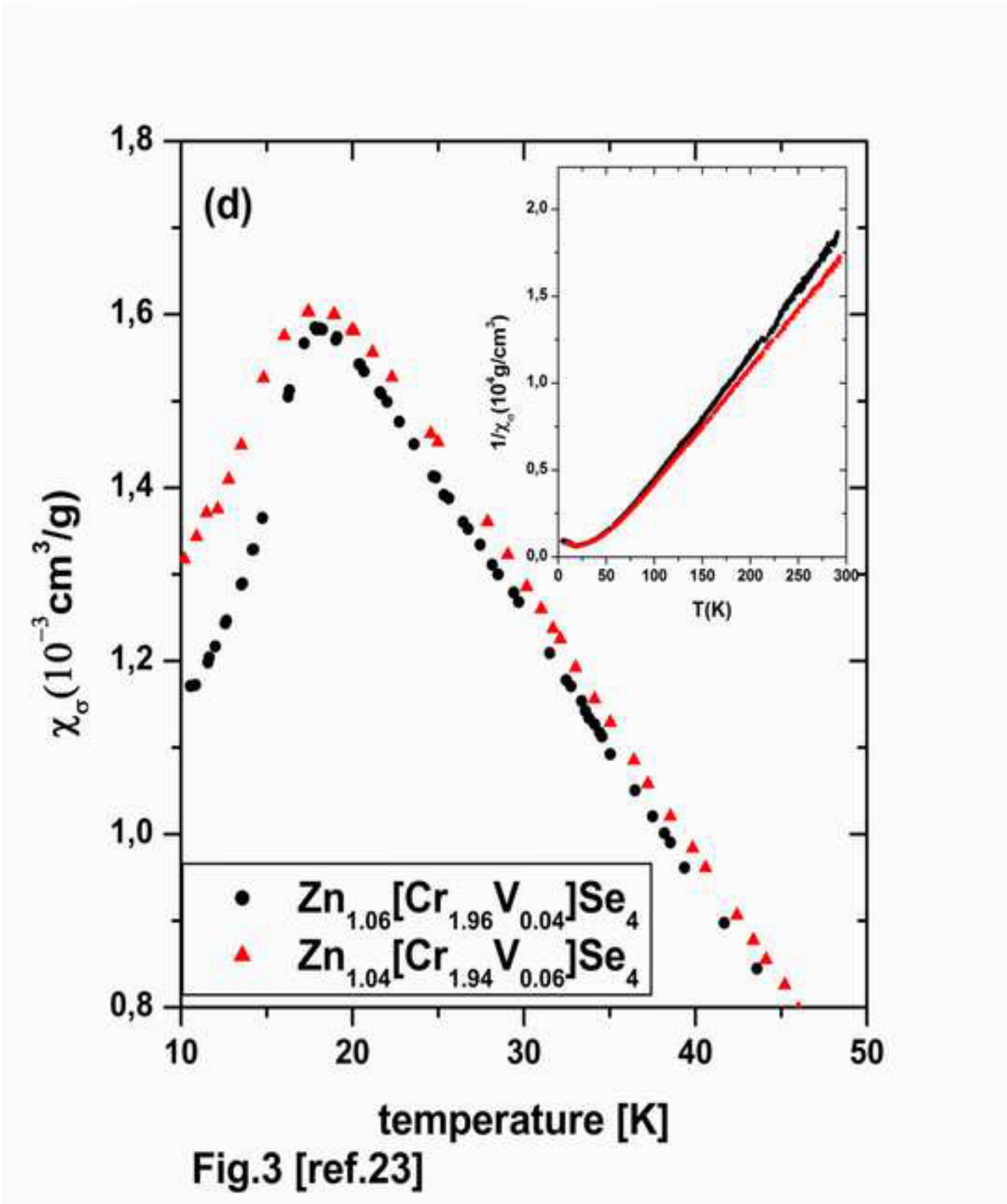


Fig.3



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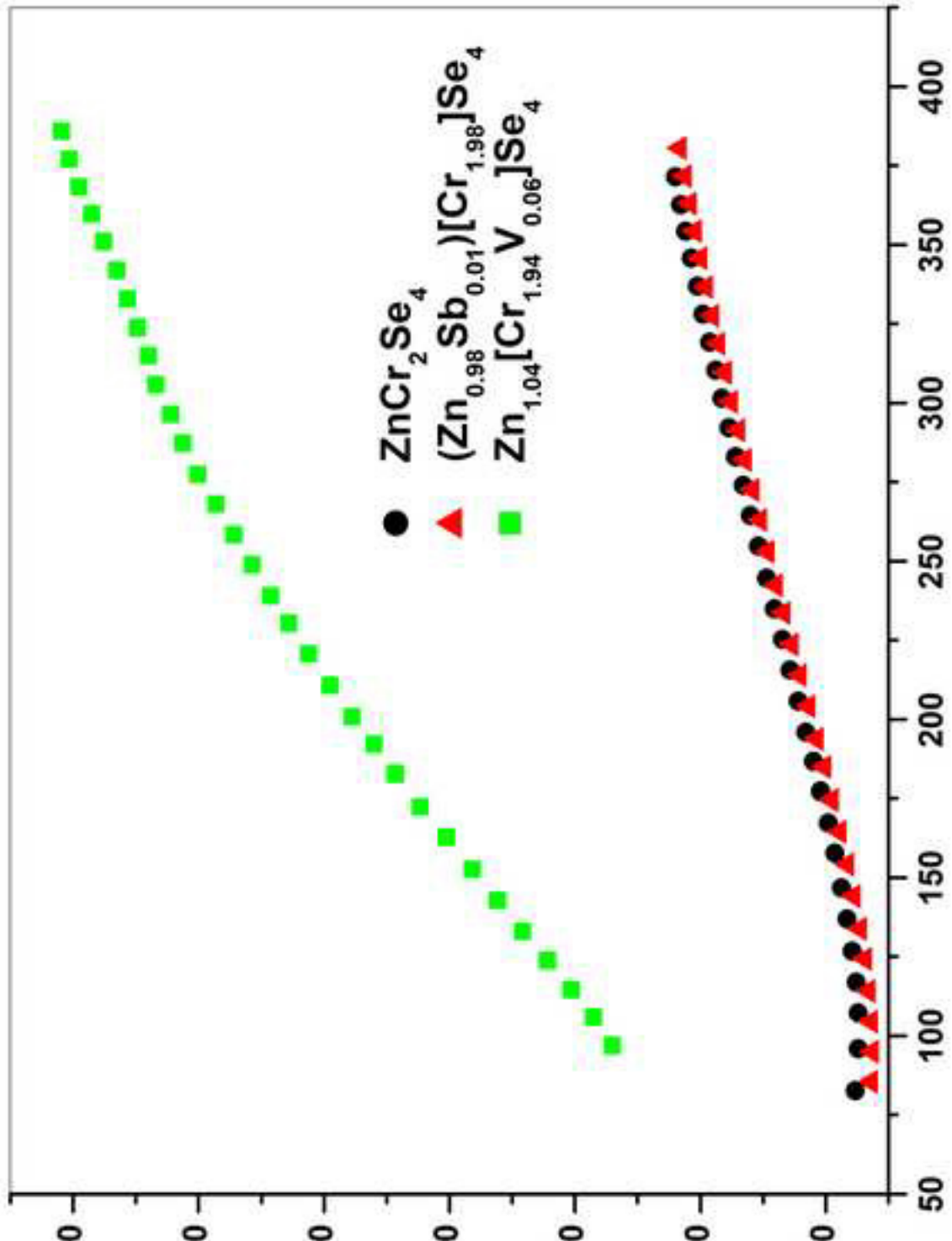

Fig.4

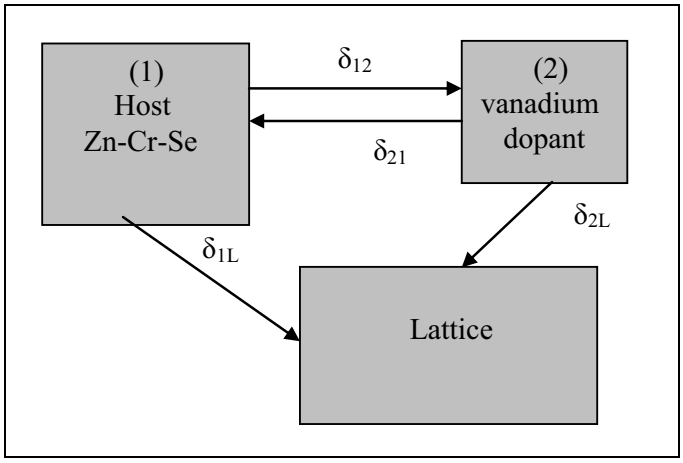

Fig.5

Table 1. EDXRF analysis for single crystals of $(Zn_{1-x}Sb_x)[Cr_{2-x/3}]Se_4$ and $(Zn)[Cr_{2-x}V_x]Se_4$

Chemical formula	Zn	Sb	V	Cr	Se
$(Zn_{0.98}Sb_{0.01})[Cr_{1.98}]Se_4$ $(Zn_{0.97}Sb_{0.02})[Cr_{1.99}]Se_4$	13.27±0.08 13.08±0.07	0.29±0.04 0.56±0.05		21.2±0.1 21.3±0.1	65.2±0.2 65.0±0.2
$(Zn_{1.06})[Cr_{1.96}V_{0.04}]Se_4$ $(Zn_{1.04})[Cr_{1.94}V_{0.06}]Se_4$	14.2±0.2 13.9±0.1		0.42±0.06 0.61±0.05	20.8±0.3 20.7±0.2	64.6±0.4 64.8±0.3

The results are in % (m/m)

Reference Number: PCS 6422

The ESR study of single crystal spinel $ZnCr_2Se_4$ diluted with Sb and V

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Research Highlights

- The preparation of single crystals of spinel $ZnCr_2Se_4$ diluted with Sb and V.
- The temperature dependence of the ESR linewidth.
- The one-phonon relaxation in paramagnetic range of Sb-doped spinel.
- The complex paramagnetic relaxation model for V-doped spinel.
- The magnetic ordering of spinel studied occurs in a two-step process.