

## Paramagnetic Resonance and Susceptibility of $\text{Li}_2\text{VSe}_2$

Yoshiyuki WATANABE

Department of Physics, Shimane University, Matsue 690

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The EPR linewidth of  $\text{V}^{2+}(\text{d}^3)$  in  $\text{Li}_2\text{VSe}_2$  has been studied. The observed temperature-dependence of linewidth shows a broad minimum around 150 K. Several mechanisms for the line broadening are examined to explain the experimental results, and the presence of a small amount of the fast relaxing  $\text{V}^{3+}(\text{d}^2)$  ions is specified as an origin of the temperature-dependent linewidth. Susceptibility data are consistent with the interpretation of EPR results.

### 1. Introduction

The intercalation process of Li in layered transition metal dichalcogenides has been widely investigated from both physical (or chemical) points of view and some practical purposes of developing new battery-materials [1-4]. The technique of Li intercalation provides a convenient tool to change the valence state of transition metals through the electron donation from Li. Most of  $\text{MX}_2$ -type dichalcogenides such as  $\text{TiS}_2$ ,  $\text{ZrSe}_2$ ,  $\text{NbSe}_2$  and  $1\text{T-TaS}_2$  react with n-butyllithium (nBuLi) and form an intercalate with the composition of  $\text{LiMX}_2$ . In these intercalates, the outer s-electrons of the guest Li in the van der Waals gap are almost completely transferred to the host as inferred *e. g.* from the absence of  $^7\text{Li}$  Knight shift [5, 6]. Such a transfer of electrons brings on a drastic change in the physical properties; electric conductivity [1], magnetic susceptibility [1] and crystal structure [1, 2].

Recently, special interests have been directed towards  $\text{VSe}_2$  because of its exceptional behaviors in the reaction with nBuLi [1, 7, 8]. In contrast with other  $\text{MX}_2$ -type dichalcogenides,  $\text{VSe}_2$  can form an intercalate  $\text{Li}_2\text{VSe}_2$  in addition to the usual one  $\text{LiVSe}_2$ . Physical properties of  $\text{Li}_2\text{VSe}_2$  are quite different from those of  $\text{LiVSe}_2$ . For example, the susceptibility of  $\text{LiVSe}_2$  is small and substantially temperature-independent, indicating that d-electrons (including those transferred from Li to V ions) are itinerant [1]. On the contrary, the susceptibility attributable to  $\text{Li}_2\text{VSe}_2$  shows a Curie-Weiss like temperature-dependence which means the existence of local moments. The Curie constant evaluated leads to an effective magnetic moment  $\mu_{\text{eff}} = 3.3 - 3.45 \mu_{\text{B}}$  ( $\mu_{\text{B}}$ : Bohr magneton) which is somewhat smaller than  $3.87 \mu_{\text{B}}$  expected for  $S=3/2$ ,  $g=2$  state ( $\text{V}^{2+}(\text{d}^3)$ ) [1, 7, 8]. Since an intermediate phase between  $\text{LiVSe}_2$  and  $\text{Li}_2\text{VSe}_2$  has not yet been found, the deviation of  $\mu_{\text{eff}}$  from  $3.87 \mu_{\text{B}}$  would be explained by assuming that the final intercalate is an admixture of the  $\text{Li}_2\text{VSe}_2$  phase with an ionic configuration of  $\text{Li}_2^+\text{V}^{2+}(\text{d}^3)\text{Se}_2^{2-}$  and the  $\text{LiVSe}_2$  phase, the Pauli type paramagnet.

Recently, however, the possibility of the existence of  $V^{3+}(d^2)$  ions with local moments was pointed out for the  $Li_2VSe_2$  phase on the basis of magnetic [7] and EPR [8] results. If an appreciable amount of  $V^{3+}(d^2)$  ions exists in the  $Li_2VSe_2$  phase, one can explain the observed small susceptibility without the coexistence of the  $LiVSe_2$  phase [7]. We discussed this problem in a previous paper [9] on the basis of data of EPR and crystal structure. In this paper, some additional data and explanations for EPR and magnetic behaviors of  $Li_2VSe_2$  are presented.

## 2. Experimental

Powder samples of  $VSe_2$  were prepared by a direct reaction of elements at  $750^\circ C$  in evacuated quartz tube with a small excess of Se.  $VSe_2$  sample thus obtained was immersed in a  $nBuLi$  hexane solution of Li content sufficient for producing  $Li_2VSe_2$ , and was sealed in a glass tube. X-band (9.5 GHz) EPR measurements were carried out for these sealed samples to avoid the influence of moistures. The EPR spectrometer is a home-made one with 2 kHz field modulation. Magnetic susceptibility was measured between 80 and 300 K with vibrating sample magnetometer (PAR155). Samples for magnetic experiments were prepared according to the same procedure as that in the previous paper [8].

## 3. Results and Discussion

We show in Fig. 1 an example of the first derivative EPR spectrum for a  $VSe_2$  powder- $nBuLi$  mixture in hexane. The spectrum which has a  $g$ -value of 1.98 has been

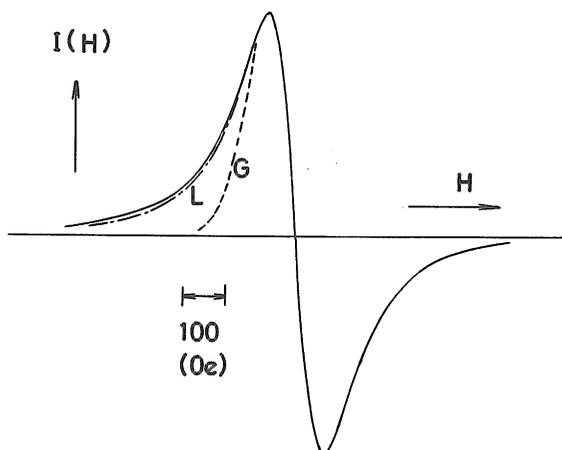


Fig. 1. A derivative EPR spectrum of  $VSe_2$  powder- $nBuLi$  mixture at 300 K. The curves designated by L or G represent the best fit one for the Lorentzian or Gaussian lineshape, respectively.

identified as due to the  $\text{V}^{2+}(\text{d}^3)$  ions within the  $\text{Li}_2\text{VSe}_2$  phase [1, 8]. The lineshape well fits to the derivative form of the Lorentzian line [10] represented by

$$I(H) = \text{const.} \frac{(H - H_0)\Delta H}{\{(H - H_0)^2 + (\Delta H/2)^2\}^2}, \quad (1)$$

where  $H_0$  is the resonance field and  $\Delta H$  is the full half-width of the absorption line. For the purpose of comparison, we show in Fig. 1 both a Lorentzian line obtained by substituting  $\Delta H = 240$  Oe into eq. (1) and a Gaussian one [10] fitted at the central part of the observed line. In view of the small value of the linewidth and the Lorentzian shape of the observed lines, it is evident that the present lines are strongly exchange-narrowed [8]. For a Lorentzian line,  $\Delta H$  is correlated to the peak-to-peak linewidth  $\Delta H_{\text{pp}}$  of the derivative curve by the relation

$$\Delta H = \sqrt{3} \Delta H_{\text{pp}}. \quad (2)$$

Figure 2 shows the observed variation of  $\Delta H_{\text{pp}}$  with the immersion time in nBuLi hexane solution. As seen in the figure,  $\Delta H_{\text{pp}}$  exhibits a marked dependence upon both the time and the reaction temperature, a decrease from  $\sim 260$  Oe at the beginning to  $\sim 120$  Oe after a completed reaction. If we take the ionic configuration of  $\text{Li}_2\text{VSe}_2$  to be  $\text{Li}_{2-y}^+\text{V}_{1-y}^{2+}(\text{d}^3)\text{V}_y^{3+}(\text{d}^2)\text{Se}_2^{2-} + \text{Li}_y$ , or  $\text{Li}_y\text{Li}_{2-y}^+\text{V}_{1-y}^{2+}(\text{d}^3)\text{V}_y^{3+}(\text{d}^2)\text{Se}_2^{2-}$  according to magnetic data [7], then the present time-dependence of the linewidth implies that the amount of  $\text{V}^{3+}(\text{d}^2)$  ions (*i. e.*  $y$ ) changes drastically with time. This conclusion is of course based on the assumption that the  $\text{V}^{3+}(\text{d}^2)$  ions are coupled strongly to lattice

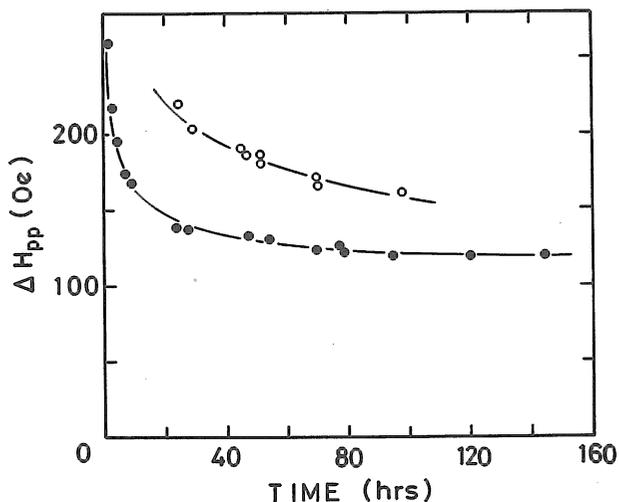


Fig. 2. The variation of the peak-to-peak linewidth  $\Delta H_{\text{pp}}$  at 300 K with the immersion time and the temperature of solution (closed circles:  $\sim 35^\circ\text{C}$  and open circles:  $< 20^\circ\text{C}$ ).

and hence these are the main origin of the observed time and temperature-dependent linewidth [8, 9, 11]. In order to examine the change in the ionic configuration of  $\text{Li}_2\text{VSe}_2$  with time, we analyzed the X-ray powder diffraction patterns at different stages of the intercalation reaction [9]. Results show, however, that there is no appreciable change in lattice parameters of  $\text{Li}_2\text{VSe}_2$  with time, indicating the absence of drastic change in the ionic configuration [9]. From these results, we concluded that the concentration of  $\text{V}^{3+}(\text{d}^2)$  ions in  $\text{Li}_2\text{VSe}_2$  should be very small.

Now, we examine the possibility that the observed time and temperature-dependent linewidth originates from some mechanisms other than that due to  $\text{V}^{3+}(\text{d}^2)$  ions considered above. For this, one should remind of the characteristic  $\Delta H_{\text{pp}}$  vs.  $T$  curve found for  $\text{V}^{2+}\text{EPR}$  in  $\text{Li}_2\text{VSe}_2$ . Figure 3 shows an example of these curves obtained at an early stage where the reaction is incomplete. The temperature-dependence of  $\Delta H_{\text{pp}}$  was well described for every stage of reaction by the formula

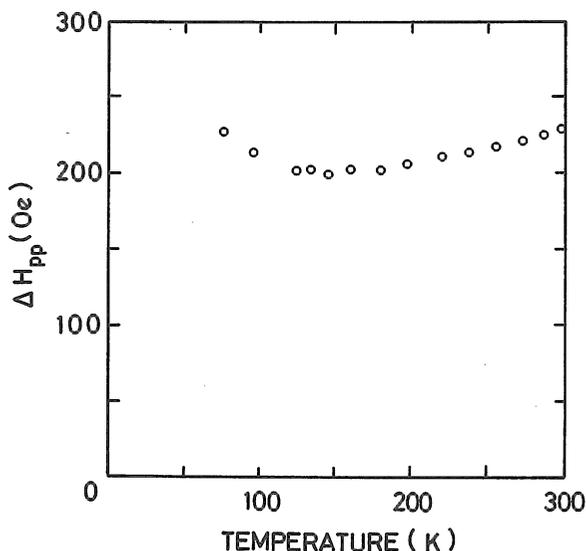


Fig. 3. A temperature-dependence of  $\Delta H_{\text{pp}}$  showing the appearance of the minimum even at an early stage of reaction. Measurements were made after 5 hrs reaction.

$$\Delta H_{\text{pp}} = C_1 + C_2 T + C_3 / T, \quad (3)$$

where  $C_1$ ,  $C_2$ ,  $C_3$  are constants [8]. Formally speaking, the curve shown in Fig. 3 is quite reminiscent of the temperature dependence of the linewidth found for two-dimensional (2d) antiferromagnets such as  $\text{K}_2\text{Mn}_c\text{Mg}_{1-c}\text{F}_4$  [12, 13] and  $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4$  [14], and also for paramagnetic ions embedded in metals (*e. g.* Gd in Pd [15]). The linewidth minimum found for 2d antiferromagnets has been explained in terms of the rise in linewidth near  $T_N$  ( $T_N$ : the critical temperature for a

long-range order), combined with the effect of short-range order in a temperature region  $T > 2T_N$  (a gradual decrease in the linewidth towards lower temperatures) [12, 13, 16]. For  $\text{Li}_2\text{VSe}_2$ , however, the temperature of the long-range order is about 20 K [1, 7] and is too low to explain the rise around 150 K in terms of the critical line broadening near  $T_N$ . In addition, the low temperature rise for the present case is remarkable for the specimen with smaller amount of ions responsible for EPR [8]. This is completely opposite to behaviors in  $\text{K}_2\text{Mn}_c\text{Mg}_{1-c}\text{F}_4$ . These seem to rule out the possibility of the long-range ordering as the origin of the  $C_3/T$  term in eq. (3). It is well known [16], furthermore, that the short range order effect at  $T > 2T_N$  in 2d ferromagnets brings on the rise in linewidth towards lower temperatures. That is, the behavior of 2d ferromagnets is opposite to that of 2d antiferromagnets such as  $\text{K}_2\text{Mn}_c\text{Mg}_{1-c}\text{F}_4$  and seems appropriate to explain the  $C_3/T$  term. In fact, some of  $\text{MX}_2$ -type dichalcogenides (*e. g.*  $\text{NaCrSe}_2$  [17]) have a ferromagnetic exchange interaction between metal ions in a hexagonal layer. However, magnetic data for  $\text{Li}_2\text{VSe}_2$  indicate the dominating exchange interaction between  $\text{V}^{2+}(\text{d}^3)$  ions in a hexagonal layer to be negative, *i. e.* an antiferromagnetic spin order in the layer [7]. The  $C_2T$  term in eq. (3) is alike to the Korringa-type line broadening for paramagnetic ions in metals, which is caused through the exchange interaction with the conduction electrons [15]. Such a similarity does not necessarily indicate, however, the presence of the interaction between  $\text{V}^{2+}(\text{d}^3)$  and itinerant d-electrons in the  $\text{LiVSe}_2$  phase. We rather point out here that the  $\text{Li}_2\text{VSe}_2$  phase accommodating  $\text{V}^{2+}(\text{d}^3)$  ions is a phase clearly separated from the coexisting  $\text{LiVSe}_2$  phase as confirmed by the X-ray powder diffraction [9]. The interaction between separated phases should be small. Thus, we come to a conclusion that some relaxation mechanisms other than those mentioned above are operating in  $\text{Li}_2\text{VSe}_2$ , being consistent with our previous interpretation [8, 9] that a small amount of the fast relaxing impurities,  $\text{V}^{3+}(\text{d}^2)$ , would be the origin of the observed linewidth.

Figure 4 shows the susceptibility for two specimens prepared under different temperature conditions. For the convenience to estimate the degree of the progress of reaction,  $\Delta H_{pp}$  values at 300 K are shown in Table I. It is evident from these values together with Fig. 2 that the reaction is incomplete for the case of the specimen (1). Here, we attempted to fit the susceptibility data to the formula

$$\chi_g = A + B/(T + \theta), \quad (4)$$

where  $A$ ,  $B$ ,  $\theta$  are constants.  $\chi_g$  vs.  $1/(T + \theta)$  curves are illustrated in the figure by assuming  $\theta = 100$  K [7] for both specimens. Agreement between the experimental data and eq. (4) is excellent and values of  $A$  and  $B$  thus obtained are shown in Table I. The fact that these two specimens have the same  $\theta$  value provides another convincing support to the previous conclusion that the  $\text{Li}_2\text{VSe}_2$  phase is locally produced even at the early stage of the reaction [8]. If the Curie-Weiss term  $B/(T + \theta)$  originates from  $\text{V}^{2+}(\text{d}^3)$  ions within the  $\text{Li}_2\text{VSe}_2$  phase, then  $B$  should be

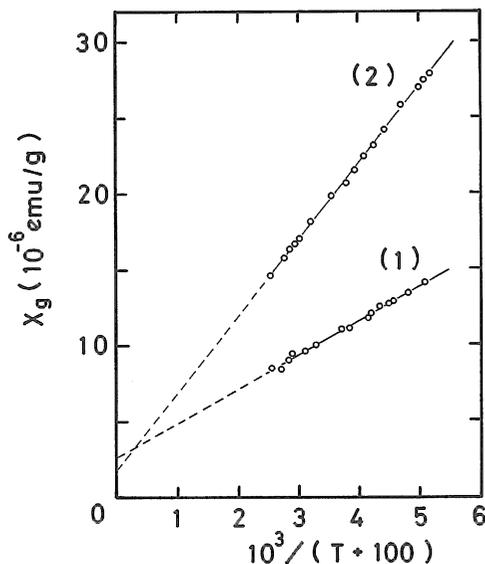


Fig. 4. Susceptibilities for two different intercalates. For the specimen (1), the intercalation is incomplete (see Table I and compare  $\Delta H_{pp}$  at 300 K to those in Fig. 2).

Table I.

No.	Reaction temperature ( $^{\circ}\text{C}$ )	$\Delta H_{pp}$ (Oe) at 300 K	$A$ $10^{-6}$ emu/g	$B$ Kemu/g	$\alpha$	$\beta$	$\alpha + \beta$
1	<20	230	2.2	2.34	0.58	0.28	0.86
2	35	140	1.7	5.04	0.45	0.60	1.05

$$B = \beta N g^2 \mu_B^2 S(S+1)/3k, \quad (5)$$

where  $g=2$ ,  $S=3/2$  and  $k$  is the Boltzmann constant and  $N$  is the total number of vanadium per unit weight of the specimen.  $\beta$  is a numerical factor between 0 and 1 that represents the ratio of the number of  $\text{V}^{2+}(\text{d}^3)$  ions to the total number of vanadium in the specimen. The values of  $\beta$  obtained from data are also shown in Table I together with  $\alpha$  defined by  $\alpha = A/\chi_g(\text{LiVSe}_2)$ , where  $\chi_g(\text{LiVSe}_2) = 3.8 \times 10^{-6}$  emu/g [1]. The  $\alpha + \beta$  value for the specimen (2) is quite close to unity ( $\alpha \sim 0.4$ ,  $\beta \sim 0.6$ ). This strongly suggests that the present intercalate is an admixture of ( $\sim 60\%$   $\text{Li}_2\text{V}^{2+}(\text{d}^3)\text{Se}_2 + \sim 40\%$

$\text{LiVSe}_2$ ), which is comparable to the composition ( $\sim 70\%$   $\text{Li}_2\text{V}^{2+}(\text{d}^3)\text{Se}_2 + \sim 30\%$   $\text{LiVSe}_2$ ) for the similar intercalate reported in literature [7]. For the specimen (1), on the other hand,  $\alpha + \beta$  is somewhat smaller than unity. But in this case, the discrepancy could be explained by the survival of the  $\text{VSe}_2$  phase with a smaller susceptibility  $\chi_g(\text{VSe}_2) = 1.5 \times 10^{-6}$  emu/g [18], which is confirmed by X-ray diffraction

in the case of the incomplete reaction. That is,  $\alpha$  for this case should be evaluated by

$$\alpha = A / \{ \lambda \chi_g(\text{LiVSe}_2) + (1 - \lambda) \chi_g(\text{VSe}_2) \}, \quad (6)$$

where  $\lambda$  denotes the relative amount of the  $\text{LiVSe}_2$  phase ( $1 > \lambda > 0$ ). If the deviation of  $\alpha + \beta$  from unity is entirely to be ascribed to the effect of the  $\text{VSe}_2$  phase, then we obtain  $\lambda \sim 0.7$  which is a plausible value. Thus, the susceptibility data are also consistent with the conclusion from EPR and X-ray results that the final intercalate  $\text{Li}_2\text{VSe}_2$  contains only a small amount of  $\text{V}^{3+}(\text{d}^2)$  ions.

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