

Intermediate-valence effects on the phase diagram of $NiS_{2-x}Se_x$

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Using a modified Falicov-Kimball model and introducing intermediate valence effects, we reproduce the phase diagram ($T-x$) of $NiS_{2-x}Se_x$. This allows us to develop a simple picture of the physical properties of these compounds based on the concepts proposed to explain the anomalies found in some rare-earth compounds.

I. INTRODUCTION

The intermediate valence (IV) concept has proved to be very useful in explaining anomalous properties of a large variety of rare earths and their compounds.¹ In this sense a particularly important property is the demagnetization produced under pressure or by alloying,^{2,3} whereby a compound expected to show some kind of localized magnetic moment appears to lose it.

As is well known, the magnetic properties of the rare earths are mainly determined by the inner 4*f* shell. In this work we explore the possibility of finding IV effects in transition-metal compounds, where the important electrons belong to the 3*d* shell. As these electrons are less screened from their surroundings⁴ than the 4*f*'s, IV effects are more difficult to identify.

$NiS_{2-x}Se_x$ ($0 \leq x \leq 2$) seems to be a good set of compounds in which to look for these effects, as we argue below. NiS_2 and $NiSe_2$ are the limit cases of the set and their properties are drastically different. NiS_2 is semiconductor at all temperatures⁵; it has localized magnetic moments at the Ni sites showing Curie susceptibility⁶ ($\mu_{eff} = 3.2\mu_B$) above 40 K, and antiferromagnetic ordering below⁷ and as all the members of the set, it has pyrite structure with lattice constant⁸ $a = 5.69 \text{ \AA}$. $NiSe_2$, on the other hand is a metal,⁹ it shows a Pauli-like susceptibility,¹⁰ indicative of a lack of the local moment; it does not have an ordered magnetic phase and its lattice constant is $a = 5.96 \text{ \AA}$.

The phase diagram^{11,12} shows the change of the properties as we go from NiS_2 to $NiSe_2$ (Fig. 1). The replacement of S by Se takes place with no change of the crystal structure, which remains pyritelike. It is striking that the exchange of two chemically similar substances (S and Se), both nonmagnetic, produces a metal-insulator transition and a reduction of the magnetic ordering temperature in the metallic phase; for $x \geq 1$ there is no magnetic order. Moreover, the fact that the measured magnetic susceptibility for $x = 2$ ($NiSe_2$) is Pauli-like shows that the static atomic moments themselves vanish or at least are strongly di-

minished. We consider the magnetic behavior to be an essential factor of the features displayed by $NiS_{2-x}Se_x$, and it compels us to introduce the IV concept to explain the demagnetization, as in the case of rare earths.

We will not take into account the existence of weak ferromagnetism (for $x \leq 0.4$). Its presence seems to be associated with nonstoichiometry, mainly when referring to the relationship between the number of Ni and S vacancies.¹³

Goodenough has discussed the band structure of pyrites¹⁴ from a general point of view, while Khan¹⁵ has calculated the band structure for FeS_2 and extended his results qualitatively to NiS_2 . Bands originating mainly from the sp^3 orbital of S_2^{2-} are either full or empty and hence are irrelevant for our model. In the band coming from the 3*d* Ni^{2+} levels (3*d* levels split into t_{2g} and e_g sublevels in the presence of the crystal field) correlation effects are extremely important. Usual band calculations do not take into ac-

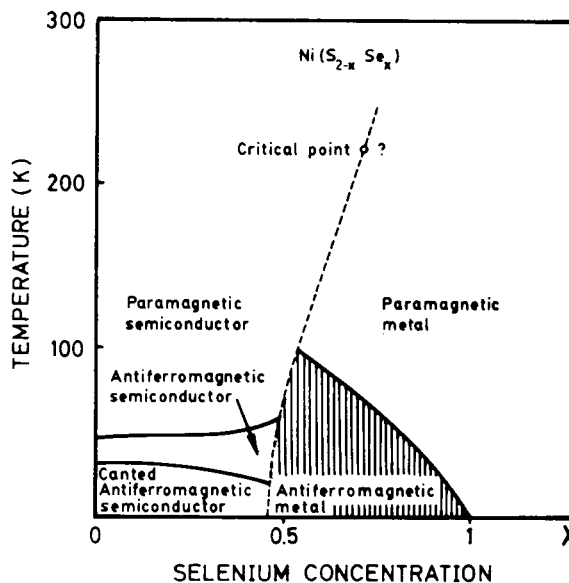


FIG. 1. $NiS_{2-x}Se_x$ schematic phase diagram obtained from Gautier *et al.* (Ref. 11).

count correlation effects and are therefore not appropriate to describe the $3d$ band.¹⁶ This shows up very clearly in NiS_2 , which should be a conductor as far as the band theory is concerned: the t_{2g} band is full (it contains six electrons), while the fourfold-degenerate e_g band is half filled by the remaining two electrons of the $3d^8 \text{Ni}^{2+}$. Experiments show instead that NiS_2 is a semiconductor; this indicates that the e_g band is split by the Coulomb repulsion leading to a Mott-insulating state. Above the e_g level there should be a broad σ -conduction band whose origin cannot be clearly established: the band calculation of Ref. 15 does not consider the $4s$ or $4p$ levels of Ni which should give rise to such a band and which could coexist in energy and mix with the sp^3 anti-bonding state.

The Fermi level is located somewhere between the e_g and the σ band.

In this paper we implement a model calculation based on the Falicov-Kimball model¹⁷ generalized to take into account three magnetic interactions and hybridization. This model has shown to be very useful in describing metal-insulator transitions when the physical system has a localized level near the conduction band.

This paper includes in Sec. II a description of the model Hamiltonian and a discussion of the approximations introduced; Sec. III the free energy derived from the (approximate) Hamiltonian; in Sec. IV the resulting phase diagram of the model is considered and applied to $\text{NiS}_{2-x}\text{Se}_x$. Finally in Sec. V we present our conclusions.

II. MODEL

As mentioned in Sec. I, we will consider a generalization of the Falicov-Kimball model that includes magnetic interactions between the spins of the localized levels, and a hybridization term that leads to an intermediate-valence interpretation of the properties of the compounds. The Falicov-Kimball model is based on the existence of a set of highly correlated localized states and an uncorrelated broad conduction band. Hence we will set up a Hamiltonian for the system that consists of:

(i) A set of localized states representing the $3d$ levels of Ni^{2+} . We will tentatively identify them with the narrow e_g band¹³ split from the t_{2g} filled band by a strong crystal field. The assumption that this is a highly correlated band is justified by the fact that NiS_2 is a Mott insulator. This assumption implies that we will consider for the localized levels only, states corresponding to the $3d^8$ ($t_{2g}^6 e_g^2$) (triply degenerate) and $3d^7$ ($t_{2g}^6 e_g$) (doubly degenerate) configurations. For shortness we will call these "spin-one" and "spin-one-half" states. We denote by $B_{i,m}^\dagger$ ($B_{i,m}$) and $B_{i,n}^\dagger$ ($B_{i,n}$) the creation (annihilation) operators for

these states,^{18,19} and

$$B_{i,m}^\dagger B_{i,n} = |i; 3d^8, m\rangle \langle i; 3d^7, n| ,$$

where i stands for the Ni^{2+} site and $m = -1, 0, \text{ or } 1$ stands for the three possible $3d^8$ states while $n = -\frac{1}{2}, \frac{1}{2}$ stands for the two possible $3d^7$ states.

Calling Δ the energy necessary to add one electron to the $3d^7$ configuration (obtaining the ground state of the completely correlated $3d^8$ configuration) the Hamiltonian for the localized states reads

$$H_{\text{loc}} = \Delta \sum_{im} B_{i,m}^\dagger B_{i,m} . \quad (2.1)$$

(ii) A set of states representing the conduction band, of energy ϵ_K and creation and annihilation operators $C_{K\sigma}^\dagger, C_{K\sigma}$. As discussed in the Introduction, it is difficult to identify from the presumed band structure the origin of these conduction states. We will tentatively refer to them as the σ band. The corresponding Hamiltonian is

$$H_{\text{band}} = \sum_{K\sigma} \epsilon_K C_{K\sigma}^\dagger C_{K\sigma} . \quad (2.2)$$

(iii) An effective repulsion between localized and band electrons. The most obvious origin for this interaction is the Coulomb repulsion, but other contributions of elastic origin can be included in the same term.²⁰ The corresponding Hamiltonian is

$$H_G = \sum_{ij\sigma} G_{ij} \left(1 + \sum_m B_{i,m}^\dagger B_{i,m} \right) C_{j\sigma}^\dagger C_{j\sigma} . \quad (2.3)$$

(iv) Magnetic couplings between spins on different sites. Since each site can be doubly or singly occupied, with corresponding $S = 1$ or $\frac{1}{2}$ spins, this part of the Hamiltonian consists of one of three terms, corresponding to spin-one-spin-one ($J_1 \vec{S} \cdot \vec{S}'$), spin-one-spin-one-half ($J_2 \vec{S} \cdot \vec{\sigma}'$), or spin-one-half-spin-one-half ($J_3 \vec{\sigma} \cdot \vec{\sigma}'$) interactions. Since all phases are essentially antiferromagnetic, probably there are large contributions of superexchange to these interactions, although conduction-electron-mediated contributions could also influence the resulting coupling constants. The magnetic interaction Hamiltonian is

$$H_{\text{mag}} = \sum_{i,\delta} J \vec{S}_i \cdot \vec{S}'_{i+\delta} , \quad (2.4)$$

where δ runs over the (magnetically relevant) nearest neighbors to site i , and the symbolic notation $J \vec{S}_i \cdot \vec{S}'_{i+\delta}$ should be understood to mean

$$J \vec{S} \cdot \vec{S}' = \begin{cases} J_1 \vec{S} \cdot \vec{S}' , \\ J_2 \vec{S} \cdot \vec{\sigma}' , \\ J_3 \vec{\sigma} \cdot \vec{\sigma}' , \end{cases}$$

depending on the kind of spin we have at sites i and $i + \delta$, respectively.

(v) A hybridization term that mixes the $3d^8$ with the $(3d^7 + \text{band})$ states by transferring one electron from the d states to the band. It is

$$H_{\text{hyb}} = \sum_{imn\sigma} V_{mn\sigma} (B_{i,m}^\dagger B_{i,n} C_{i\sigma} + C_{i\sigma}^\dagger B_{i,n}^\dagger B_{i,m}) . \quad (2.5)$$

The effect of this term is to introduce a noninteger occupation of the $3d$ levels, as can be seen from the fact that the number of d electrons ceases to be a good quantum number. Furthermore, it produces a demagnetization of the $3d$ levels. Precisely this last effect is in our opinion a key feature of the (Se-rich) compounds under study.

In order to make progress in the solution of the resulting very complicated Hamiltonian, we will make use of two approximations:

(a) Terms (2.3) and (2.4) will be treated in the mean-field approximation. This procedure reduces H_G to

$$H_G^{\text{eff}} = Gn \sum_{j\sigma} C_{j\sigma}^\dagger C_{j\sigma} + Gn_B \sum_{im} B_{i,m}^\dagger B_{i,m} - GNn_B , \quad (2.6)$$

where

$$G = \sum_i G_{ij} = \sum_j G_{ij} ,$$

$$n = \sum_m \langle B_{i,m}^\dagger B_{i,m} \rangle ,$$

$$n_B = \sum_\sigma \langle C_{i\sigma}^\dagger C_{i\sigma} \rangle = 1 - n .$$

N is the number of lattice sites. The magnetic part is

$$\begin{aligned} H_{\text{mag}}^{\text{eff}} = & -2J_1 \delta n S \sum_i S_{iz} + J_1 \delta n^2 N S^2 - J_2 \delta (1-n) \sigma \sum_i S_{iz} \\ & - J_2 \delta n S \sum_i \sigma_{iz} + J_2 \delta n (1-n) N \sigma S \\ & - 2J_3 \delta (1-n) \sigma \sum_i \sigma_{iz} + J_3 \delta (1-n)^2 N \sigma^2 , \quad (2.7) \end{aligned}$$

where

$$S = \langle S_{iz} \rangle , \quad \sigma = \langle \sigma_{iz} \rangle ,$$

and δ is the number of (magnetically relevant) nearest Ni neighbors to each Ni site; henceforth we will replace δJ_i simply by J_i ($i = 1, 2, 3$).

(b) We assume that the main effect of the hybridization term is to introduce a lifetime for the $3d$ levels. This leads to an intermediate valence behavior; the consequences of this assumption on the physical properties have been treated by one of the authors.^{19,21} On the other hand Sales and Wohleben²² proposed for the physical properties of intermediate-valence systems, a simple ansatz which consists of replacing the real temperature T by an effective temperature $T^{\text{eff}} \equiv T + \Gamma$. The numerical consequences of both assumptions are similar if one takes Γ to be of the order of the inverse lifetime.^{19,21}

For simplicity we will use in our numerical calculations the ansatz of Sales and Wohleben. Consequently the model Hamiltonian does not contain the hybridization terms explicitly. This term is included in our calculation by replacing T by T^{eff} in the expression for the free energy derived from the model Hamiltonian.

After all these approximations our actual model Hamiltonian reduces to

$$H^{\text{eff}} = H_{\text{loc}} + H_{\text{band}} + H_G^{\text{eff}} + H_{\text{mag}}^{\text{eff}} . \quad (2.8)$$

This allows us to calculate the corresponding free energy in terms of n , S , and σ , where the effect of hybridization will be included.

III. FREE ENERGY

The model Hamiltonian allows us to write the free energy for our system. The form used here is valid for a square density of states²³; furthermore we neglect the conduction-band entropy: this approximation is valid whenever $T/W \ll 1$ (W is the bandwidth) and amounts to taking a $T=0$ Fermi distribution, $f(\epsilon)$ to calculate the free energy of the band. The resulting free energy per site is

$$\begin{aligned} F = \mathcal{E} - TS = & En - Bn^2 - J_3 \sigma^2 + \left(\frac{1}{3} W + \Delta + G\right) \\ & + T \left\{ [n \ln(n) + (1-n) \ln(1-n)] \right. \\ & \left. - n \left(\ln 3 - \int_0^S B_1^{-1}(m) dm \right) \right. \\ & \left. - (1-n) \left(\ln 2 - \int_0^{2\sigma} B_{1/2}^{-1}(m) dm \right) \right\} , \quad (3.1) \end{aligned}$$

where

$$E = E' - J_2 S \sigma + 2J_3 \sigma^2 , \quad (3.2)$$

$$B = B' + J_1 S^2 - J_2 S \sigma + J_3 \sigma^2 , \quad (3.3)$$

with

$$E' = \Delta + G - \frac{1}{2} W ,$$

$$B' = G - \frac{1}{4} W ,$$

and B_J^{-1} is the inverse Brillouin function corresponding to angular momentum J . The factor $\ln(2J+1)$ measures the entropy associated with a free ion, and the integral of B_J^{-1} takes into account the magnetic ordering. Equation (3.1) is a generalization for two magnetically ordered phases, of the free energy obtained in Ref. 23; notice that for $S = \sigma = 0$ Eq. (3.1) reduces to the normal expression for the Falicov-Kimball model with a square band.

The nonmagnetic part of the energy \mathcal{E} per site is

$$\begin{aligned}\mathcal{E}_{\text{nonmag}} &= \frac{1}{N} \int_0^\infty D(\epsilon) f(\epsilon) d\epsilon \\ &+ \Delta \sum_m \langle B_{i,m}^\dagger B_{i,m} \rangle + \langle H_G^{\text{eff}} \rangle \\ &= E'n - B'n^2 + \left(\frac{1}{4}W + \Delta + G\right) .\end{aligned}\quad (3.4)$$

$D(E)$ is the density of states. The introduction of the magnetic energy, $\langle H_{\text{mag}}^{\text{eff}} \rangle$, corresponds to the replacements $E' \rightarrow E$, $B' \rightarrow B$ and subtraction of $J_3\sigma^2$.

As mentioned before we introduce our intermediate valence assumption at this point, namely: we replace T in Eq. (3.1) by $T + \Gamma = T^{\text{eff}}$. When applying the model to a specific system such as $\text{NiS}_{2-x}\text{Se}_x$, the different parameters appearing in the expression of the free energy will generally be functions of the concentration x .

IV. PHASE DIAGRAM

A. General

By minimizing the free energy F with respect to the order parameters n , S , and σ , we obtain the (T/B) vs (E/B) phase diagram shown in Fig. 2. Our characterization of the metallic and insulating phases is as follows: at temperatures smaller than the critical temperature T_c , the free energy as a function of n shows two minima n_1 , n_2 for each value (E/B) , say $n_1 < n_2$. When the absolute minimum of F is at

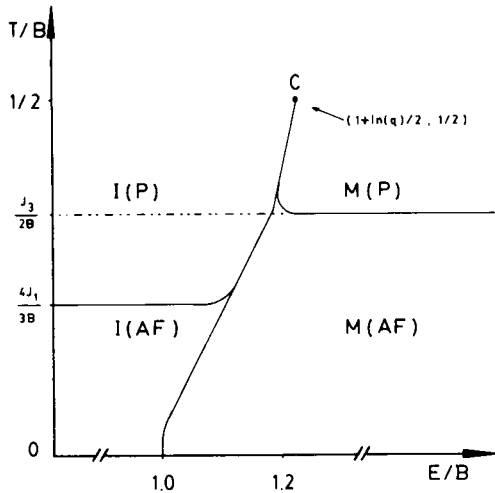


FIG. 2. Theoretical phase diagram without IV effects. It contains four different phases: M, I, P, AF denoting metal, insulator, paramagnetic, and antiferromagnetic, respectively. The values of the magnetic interactions J_i , were chosen in such a way that the critical point c has higher temperature T_c , than any of the ordered magnetic phases.

$n_1(n_2)$, we will say that the system is in the metallic (insulating) phase. For $T=0$ this gives, simply,

$$\begin{aligned}n &= 0 (n_B = 1) \text{ metal} , \\ n &= 1 (n_B = 0) \text{ insulator} .\end{aligned}$$

The following features of the phase diagram should be pointed out: (a) there are four different phases: (i) a paramagnetic (P) insulator (I); (ii) an antiferromagnetic (AF) insulator; (iii) an AF metal (M); and (iv) a paramagnetic metal. (b) The MI first-order transition line ends at a critical point C . This is a consequence of the configurational entropy [term in small square brackets in Eq. (3.1)]: because of this term, as $T \rightarrow T_c$, n_1 and n_2 both approach $n_c = \frac{1}{2}$. (c) The MI transition line below T_c but above the magnetic ordering temperatures, has positive slope. This ensures that the region above it corresponds to the insulating phase. Physically this is due to the fact that the spin value assigned to it is bigger than the metallic one.

B. $\text{NiS}_{2-x}\text{Se}_x$

Here we apply our model to $\text{NiS}_{2-x}\text{Se}_x$. In order to adjust the phase diagram obtained from the model to the experimental one, we use relations obtained by Alascio *et al.*²³ In their work, the MI transition temperature in the magnetically disordered high-temperature region was shown to be (in our notation)

$$T_f^{\text{eff}} = T_T + \Gamma = \frac{(E' - B')}{\ln \frac{3}{2}} ,\quad (4.1)$$

where T_T is the real transition temperature. Moreover, the critical-point condition reads

$$E'_c = T_c^{\text{eff}}(2 + \ln \frac{3}{2}) ,\quad (4.2)$$

where E'_c denotes the value of $E'(x)$ for $x = x_c$.

We have used data from the three published experimental phase diagrams.^{11,12} It should be noticed that there is no complete agreement between these works. Moreover, the experimental picture is not yet clear enough to fix all the variables. This is especially true of the magnetic order aspects. Because of this situation, we will take a reasonable value for J_2 ($J_2 = 550$ K), and assume E' to be constant, in order to show that it is possible to obtain good agreement between the experimental and theoretical phase diagrams.²⁴

Specifically, we use $T_T = (731x - 302)$ K; where T_T is the metal-insulator transition temperature over the ordered magnetic phases, as well as the critical-point coordinates $T_c = 137$ K, and $x_c = 0.6$. For $x = 0$, i.e., NiS_2 , the magnetic ordering temperature is $T_M = 40$ K. Finally, along the boundary line between the AF and P metallic phases, T_M decreases linearly from $T_M = 100$ K at $x = 0.55$ to $T_M = 30$ K at $x = 0.9$. For

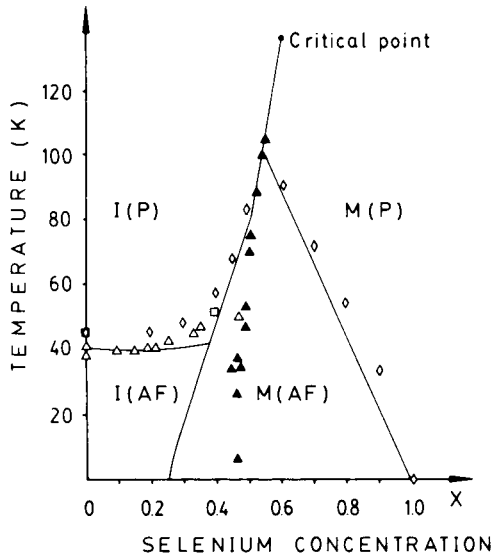


FIG. 3. Theoretical $\text{NiS}_{2-x}\text{Se}_x$ phase diagram; we also show experimental points: \blacktriangle \triangle Jarrett *et al.* (Ref. 12); \blacksquare \square Gautier *et al.* (Ref. 11); \diamond Czjzek *et al.* (Ref. 11). Filled and empty symbols denotes MI and magnetic transitions, respectively.

$x = 1$, T_M vanishes.

We assume that Γ follows the law $\Gamma = 222x$, this being the simplest possible assumption we can make to introduce the demagnetization via the intermediate valence effect. This behavior is strongly suggested by the experimental linear demagnetization mentioned above.

Considerations about the magnetic transition temperature,²⁵ help us to choose the values $J_1 = \frac{3}{4}(222x + 40)$ K and $J_3 = 444$ K. Then from Eqs. (4.1) and (4.2) we obtain $E' = 649$ K and $B' = (-386x + 772)$ K. After all these considerations, we get the phase diagram illustrated in Fig. 3. As it can be seen, there is an acceptable agreement with the experimental one.

From the free-energy expression, it is very easy to obtain (in the limit $n \rightarrow 1$) the law $n_B \approx \exp[(E - 2B)/T]$. Hence the energy gap at zero temperature is $\Delta_{\text{gap}} = 2(2B - E)$. For NiS_2 we get $\Delta_{\text{gap}} \approx 0.12$ eV. This is of the order of the gap obtained by Kautz *et al.*²⁶ It should be pointed out, however, that we have used for $J_2(x=0)$ the value 550 K, which is appropriate around $x \approx 0.5$.

V. DISCUSSIONS AND CONCLUSIONS

In Sec. IV we have shown that it is possible to obtain a phase diagram similar to that of the $\text{NiS}_{2-x}\text{Se}_x$ compounds based on the ideas contained in the Falicov-Kimball model (coexistence of localized and extended states), provided we complement it with magnetic interactions. Furthermore we have to intro-

duce the concepts developed for rare-earth compounds to explain the fact that the static magnetic moments of the system vanish.

Although the choice of parameters as functions of Se concentration is not unique, we believe that the description we propose for this set of compounds is a good approximation to reality in term of fundamental and simple concepts. The remaining ambiguities in the choice of parameters could be eliminated by studying the physical properties of the different phases. More experimental data are needed for this purpose, in particular, measurements of the magnetic susceptibility and inelastic neutron scattering in the metallic phase.

The use of the Sales and Wohlleben's ansatz introduces some inaccuracies in the theoretical phase diagram, particularly at low temperature, where it predicts finite entropy. The consequence of this is that the slope of the phase boundary lines do not go to infinity when the temperature is lowered. The general features of the phase diagram are consistent, however, with other approaches to the problem.²⁷

The idea of applying IV concepts to transition-metal solids is not new. Wohlleben and Coles³ have interpreted magnetic anomalies of transition-metal alloys, as arising from valence fluctuations at the $3d$ shell. The phase diagram of V_2O_3 under pressure and of $(\text{V}_{1-x}\text{Cr}_x)_2\text{O}_3$, and the physical properties of the metallic phases of these systems strongly suggest the presence of IV effects.

In our model, the phase change implies a strong variation of the gap between the $3d$ levels and the conduction band. Since magnetic interactions J_i are expected to be gap dependent according to Koiller-Falicov,¹⁶ it would be highly desirable to calculate them using their theory. Unfortunately, band calculations are not available for NiS_2 nor for NiSe_2 ; a detailed determination of the magnetic structure would also be useful.²⁸

The phase diagram of $\text{NiS}_{2-x}\text{Se}_x$ has been compared¹¹ to the theoretical phase diagram obtained by Cyrot.²⁹ However, since this theoretical model is devised for the case of one electron per local site, it seems too far fetched to compare its predictions with the phase diagrams obtained from $\text{NiS}_{2-x}\text{Se}_x$ or V_2O_3 .

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- ¹V. Alascio, in *Valence Instability and Related Narrow Band Phenomena*, edited by R. D. Parks (Plenum, New York, 1977).
- ²M. B. Maple and D. K. Wohlleben, in *Magnetism and Magnetic Materials, 1973*, edited by C. D. Graham, Jr., and J. J. Rhyne, AIP Conf. Proc. No. 18 (AIP, New York, 1974), p. 447.
- ³D. K. Wohlleben and B. Coles, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1973), Vol. 5, Chap. 1, and references listed therein.
- ⁴C. Kittel, *Introduction to Solid State Physics*, 4th ed. (Wiley, New York, 1971), p. 438.
- ⁵R. J. Bouchard, J. L. Gillson, and H. S. Jarrett, *Mater. Res. Bull.* **8**, 489 (1973).
- ⁶R. Benoit, *J. Chim. Phys.* **52**, 119 (1955).
- ⁷J. M. Hastings and L. M. Corliss, *IBM J. Res. Dev.* **14**, 227 (1970).
- ⁸R. J. Bouchard, *J. Cryst. Growth* **2**, 40 (1968).
- ⁹F. Hulliger, *Helv. Phys. Acta* **32**, 615 (1959).
- ¹⁰S. Furuseth, A. Kjekshus, and A. F. Andersen, *Acta Chem. Scand.* **23**, 2325 (1969).
- ¹¹F. Gautier, G. Krill, M. F. Lapierre, P. Panissod, C. Robert, G. Czjzek, J. Fink, and H. Schmidt, *Phys. Lett. A* **53**, 31 (1975); G. Czjzek, J. Fink, H. Schmidt, G. Krill, M. F. Lapierre, P. Panissod, F. Gautier, and C. Robert, *J. Magn. Magn. Mater.* **3**, 58 (1976).
- ¹²H. S. Jarrett, R. J. Bouchard, J. L. Gillson, G. A. Jones, S. M. Marcus, and J. F. Weiher, *Mater. Res. Bull.* **8**, 877 (1973).
- ¹³G. Krill, M. F. Lapierre, F. Gautier, C. Robert, G. Czjzek, J. Fink, and H. Schmidt, *J. Phys. C* **9**, 761 (1976).
- ¹⁴J. B. Goodenough, *J. Solid State Chem.* **3**, 26 (1971); **5**, 144 (1972).
- ¹⁵M. A. Khan, *J. Phys. C* **9**, 81 (1976).
- ¹⁶B. Koiller and L. M. Falicov, *J. Phys. C* **7**, 299 (1974); **8**, 695 (1975).
- ¹⁷L. M. Falicov and J. C. Kimball, *Phys. Rev. Lett.* **22**, 997 (1969).
- ¹⁸M. E. Foglio, *Rev. Mex. Fis.* **17**, 137 (1969); *J. Phys. C* **11**, 4171 (1978); *Phys. Status Solidi B* **87**, 87 (1978).
- ¹⁹B. Alascio, in *Valence Instability and Related Narrow Band Phenomena*, edited by R. D. Parks (Plenum, New York, 1977), p. 247.
- ²⁰P. W. Anderson and S. T. Chui, *Phys. Rev. B* **9**, 3229 (1974).
- ²¹B. Alascio, *Solid State Commun.* **16**, 717 (1975).
- ²²B. C. Sales and D. K. Wohlleben, *Phys. Rev. Lett.* **35**, 1240 (1975).
- ²³B. Alascio, V. Grünfeld, and A. López, *Phys. Rev. B* **5**, 3708 (1972).
- ²⁴It is possible to approximate J_2 by a constant because it turns out to be relevant only in a rather small zone around the MI transition line; this behavior is a consequence of the mean-field approximation used, and it can be seen to be related with the fact that J_2 is multiplied by the factor $n(1-n)$ in the free energy [Eq. (3.1)].
- ²⁵The magnetic transition temperature T_M can be obtained by considering the behavior of $\partial F/\partial S = \partial F/\partial \sigma = 0$, when S and $\sigma \rightarrow 0$. It can be seen to be
- $$T_M = \frac{2}{3}J_1n + \frac{1}{4}(1-n)J_3 + \left\{ \left[\frac{2}{3}J_1n - \frac{1}{4}(1-n)J_3 \right]^2 + \frac{1}{4} \left(\frac{2}{3} \right) n(1-n)J_2^2 \right\}^{1/2}$$
- Particularly useful values are
- $$T_M = \begin{cases} \frac{4}{3}J_1 & \text{if } n \rightarrow 1 \\ \frac{1}{2}J_3 & \text{if } n \rightarrow 0 \end{cases}$$
- ²⁶R. L. Kautz, M. S. Dresselhaus, D. Adler, and A. Linz, *Phys. Rev. B* **6**, 2078 (1972).
- ²⁷B. Alascio, H. Wío, and A. López, *Z. Phys. B* **36**, 37 (1979); C. E. T. Goncalves da Silva and L. M. Falicov, *Solid State Commun.* **17**, 1521 (1975); B. Alascio, A. López, and C. F. E. Olmedo, *J. Phys. F* **3**, 1324 (1973).
- ²⁸T. Miyadai, K. Takizawa, H. Nagata, H. Ito, S. Miyahara, and K. Hirakawa, *J. Phys. Soc. Jpn.* **38**, 115 (1975); T. Miyadai, K. Kikuchi, and Y. Ito, *Physica (Utrecht) B* **86-88**, 901 (1976).
- ²⁹M. Cyrot, *J. Phys. (Paris)* **33**, 125 (1972).