Large resistivity change and phase transition in LiMnAs

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I. INTRODUCTION

The idea of using semiconductors in spintronic devices has stimulated a new field of research. This is because by using not only the charge of the electron, but also its spin, to store and manipulate information has led to a new paradigm in condensed matter research to overcome the limitations set by Moore’s law. Unfortunately, semiconductivity and ferromagnetism above room temperature are not compatible. Presently, to circumvent this issue, diluted magnetic semiconductors such as GaMnAs and LiZnMnAs are used. Recently, the use of antiferromagnetic (AFM) semiconductors has been proposed, because they have a higher magnetic ordering temperature compared to diluted magnetic semiconductors. One promising candidate material for new spintronic applications is LiMnAs, given its suitable band gap and high magnetic moment per Mn atom. It was demonstrated that epitaxially grown LiMnAs thin films also show semiconducting behavior and their AFM ordering has been confirmed as well. Thus, LiMnAs, LaOMnAs, and related materials allow for the study and development of new AFM semiconductors, and the compounds are also interesting from a purely academic viewpoint. CuMnAs has also been suggested as an alternative semiconducting AFM material; however, this compound shows semimetallic behavior in contrast to the desired semiconducting properties. Still, the compounds with the general formula AMnX, where A = Li, Ni, Cu, or LaO and X = As or Sb offer a good starting point for the development of novel semiconducting magnetic materials for applications in devices such as single-electron transistors.

In the ground state, both LiMnAs and LaOMnAs show AFM insulating behavior. Chemically, LiMnAs consists of ionic Li+ and tetrahedral [MnAs]− layers (see Fig. 1), with Mn2+ in a d5 and As3− in a nominal s2p6 closed shell configuration. LiMnAs is isostructural to LiFeAs superconductor. Structurally, LaOMnAs is closely related to LiMnAs (see Figure 1) and to the LaFeAs layered superconductor. In comparison to LiMnAs, where the Mn moments are ordered antiferromagnetically both in the ab Mn planes and between the Mn planes stacked along the c axis in the case of LaOMnAs, the moments are aligned antiferromagnetically in the ab plane but ferromagnetically along c.

Interestingly, in contrast to the expected 5 μB of the S = 5/2 Mn2+ ion, neutron scattering data on LiMnAs and LaOMnAs suggests a magnetic moment of approximately 3.4 to 3.8 μB, which is close to the magnetic moment of 4 μB for an S = 2 Mn3+ ion. This closely resembles the simple rules and general observation made...
We discuss the electronic and magnetic properties of LiMnAs and LaOMnAs, including their transport properties from the tetragonal to a cubic phase. In addition, it was noted in Ref. 19 that in the MnAs series derived from neutron diffraction measurements on AMnAs compounds, where A is an alkali metal.

Before turning to the presentation of our results, in Table I first we provide a general overview of the most important characteristics and material properties of various compounds for the aforementioned AMnX class, with A = Li, LaO. Table I serves as a set of reference values, providing a solid basis of comparison with our measured data for LiMnAs and LaOMnAs, using which we can derive more general conclusions that are applicable to the entire family. As the data in Table I show, the materials in the AMnX family can be classified into two main categories: those that are semiconducting or semi-metallic with AFM ordering, and those which are metallic or half-metallic and ferromagnetic (FM). There is a correlation between the local moments of Mn and the Mn–Mn distances ($d_{\text{Mn–Mn}}$). That is, a shorter $d_{\text{Mn–Mn}}$ results in lower moment of Mn. The $d_{\text{Mn–Mn}}$ distance plays a major role in the magnetism of these compounds, whose behavior is transferable to LiMnAs, LaOMnAs, and other materials. The structural and magnetic data for the AMnAs series derived from neutron diffraction measurements is collected from the literature in Table I.

II. RESULTS AND DISCUSSION

In Ref. 19 it was already noted, that in the AMnX series, where A is an alkali metal, and X is an element from the 15th group of the periodic table, there is a correlation between the local moments of Mn and the Mn–Mn distances ($d_{\text{Mn–Mn}}$). That is, a shorter $d_{\text{Mn–Mn}}$ results in lower moment of Mn. The $d_{\text{Mn–Mn}}$ distance plays a major role in the magnetism of these compounds, whose behavior is transferable to LiMnAs, LaOMnAs, and other materials. The structural and magnetic data for the AMnAs series derived from neutron diffraction measurements is collected from the literature in Table I.

In this work, we elaborate on the synthesis and bulk characterization of polycrystalline LiMnAs and LaOMnAs, and compare their properties to other related compounds based on a short review from the literature on the AMnX family. We show that LiMnAs can undergo a first-order phase transition from the tetragonal to a cubic phase. In addition, we discuss the electronic and magnetic properties of LiMnAs and LaOMnAs, including their transport properties. By combining ab-initio density functional theory (DFT) calculations with our experiments, we discuss the electronic structure and magnetic exchange coupling of the Mn atoms, further commenting on the non-Curie-Weiss-like behavior experimentally reported for related compounds. We also address an open question arising from a previous work, regarding the weak ferromagnetic behavior observed in LaOMnAs, which so far has been attributed to a small spin canting. However, thus far, it was not taken into consideration that the formation of small amounts of MnAs as impurities during synthesis ($\leq 1\%$) cannot be excluded completely, and this could explain the weak ferromagnetic behavior.

![FIG. 1. (color online) Crystal and magnetic structure of LiMnAs and LaOMnAs. The blue arrows indicate the direction of the magnetic moments of the Mn atoms.](image-url)
TABLE II. Structural, electronic and magnetic properties of various AMnX based compounds, where A = Li, Ni, Cu, or LaO and X = As or Sb, and the binary MnAs compound. The shortest Mn–Mn distance is given by \(d_{\text{Mn–Mn}}\).

| Compound  | Electronic structure | Magnetic order | Mn magnetic moment [\(\mu_B\)] | \(d_{\text{Mn–Mn}}\) [\(\text{Å}\)] | Space group | Literature |
|-----------|----------------------|----------------|-------------------------------|----------------------------------|-------------|------------|
| LiMnAs    | semiconductor        | AFM            | 3.8                           | 3.008                            | \(P4/nmm\) (tetragonal)         | this work and Ref. 12 |
| CuMnAs    | semimetal            | AFM            | no data                       | 3.452                            | \(Pnma\) (orthorh.)             | Ref. 9       |
| CuMnSb    | semimetal            | AFM            | 3.9                           | 4.301                            | \(F\bar{4}3m\) (cubic)          | Refs. 9 and 20 |
| LaOMnAs   | semiconductor        | AFM            | 3.34                          | 2.914                            | \(P4/nmm\) (tetragonal)         | Refs. 13 and 21 |
| NiMnAs    | half metallic-       | FM             | 4.0                           | 4.051                            | \(F\bar{4}3m\) (cubic)          | Ref. 22      |
| NiMnSb    | half metallic-       | FM             | 4.0                           | 4.186                            | \(F\bar{4}3m\) (cubic)          | Refs. 20 and 23 |
| MnAs      | metallic             | FM             | 3.4                           | 3.730                            | \(P6_3/mmc\) (hexagonal)        | Refs. 24 and 25 |

A. Synthesis

LiMnAs was synthesized and characterized as bulk material in the 1980s\(^{12,27}\) by a high-temperature reaction of the elements lithium, manganese, and arsenic. It was found that this compound is AFM-ordered, where the Néel temperature is approximately 400 K, but the exact Néel temperature is not known.

Using a similar synthesis route, our preliminary experiments revealed a number of small Bragg reflections in powder X-ray diffraction (XRD) patterns of the target compound caused by impurities. These Bragg peaks become significantly stronger with increasing temperature and reaction time and stem from an attack of the tantalum ampoule by arsenic. Therefore, LiMnAs was prepared as follows: mixtures of stoichiometric amounts of Li (foil), Mn (chips) and As (pieces) (all 99.999% purity) were placed in Al\(_2\)O\(_3\) crucibles. The total mass was approximately 2 g per sample. Each crucible was enclosed in an arc-sealed tantalum ampoule at 300 mbar Ar, which in turn was jacketed by an evacuated fused silica ampoule. A grey powder was obtained after heating the mixtures to 1423 K with a low heating rate of 1 K/min in a muffle furnace. This temperature was maintained for 2 h and then reduced to 1173 K. After 24 h, the ampoules were quenched in water. All of the handling was performed in a glove-box under Ar (\(p(O_2,H_2O)\) \(\leq 1\) ppm). LaOMnAs was synthesized from the starting materials LaAs, Mn, and MnO\(_2\) in stoichiometric amounts at 1423 K for 42 h in an Al\(_2\)O\(_3\) crucible, which was in turn enclosed in an evacuated and fused silica tube.

B. Crystal and magnetic structure

Powder X-ray diffraction (XRD) of the final product showed single-phase LiMnAs. The powder diffraction experiment was performed with Cu K\(_{\alpha 1}\) radiation (\(\lambda = 1.5406\) Å) in Debye-Scherrer geometry. The sample was sealed in a glass capillary with a 0.3 mm diameter. A representative XRD pattern obtained at 293 K is shown in Figure 2 with a Rietveld refinement carried out using Jana 2006\(^{28}\). LiMnAs has a tetragonal unit cell with \(a = 4.2555(1)\) Å and \(c = 6.1641(2)\) Å (\(P4/nmm\), \(Z = 2\), Li on 2\(b\), Mn on 2\(a\), As on 2\(c\) and \(z(\text{As}) = 0.7575(2)\)) in agreement with the older reports.

Chemical analyses for non-metal impurities were carried out using the carrier gas hot extraction or the combustion technique (TCH 600, C 200 (LECO\(^\text{R}\)⃝)). For all samples, the impurities were below the limit of detection (LOD in ppm): H(100), N(200), O(1000) and C(1500) based on 20 mg initial weight. The 1:1:1 target composition was checked by Inductively-Coupled-Plasma-Optical Emission Spectrometry (ICP-OES; Vista RL, Varian) resulting in Li:Mn:As = 1.03(1):0.98(1):0.99(1).

A specimen for metallographic examination was prepared from one sample. Because of moisture and air sensitivity, this was carried out in a glove-box using...
Figure 2. (color online) The observed X-ray powder diffraction pattern (points) and the fit from the Rietveld refinement (solid line) of LiMnAs at 293 K. The Bragg reflection marker and the difference curve are shown at the bottom. The inset shows the tetragonal crystal structure highlighting slabs of edge-connected MnAs tetrahedra stacked along the c-axis.

Specific heat measurements of LiMnAs in the temperature range of 240–780 K revealed only one DSC peak (see Figure 3a) corresponding to a reversible phase transition with onset temperature $T_o = 768$ K. To identify the nature of this phase transition, temperature-dependent powder XRD was performed with a Stoe STADI II diffractometer with Mo Kα$_1$ radiation. The powder (20–50 µm) was sealed in a 0.5 mm quartz glass capillary. The measurements were carried out in the range from 323 K to 873 K in steps of 50 K. The observed powder patterns are shown in the range of $14^\circ \leq 2\theta \leq 25^\circ$ in Figure 4. All powder patterns up to 723 K can be indexed based on a tetragonal unit cell, whereas the powder patterns at 823 K and 873 K are indexed based on a cubic unit cell with $a_{\text{cub}} \approx c_{\text{tet}} \approx a_{\text{tet}} \sqrt{2}$. The high-temperature phase, HT-LiMnAs, crystallizes in MgAgAs structure type ($F\overline{4}3m$, $Z = 4$, Li on 4b, Mn on 4a and As on 4c) according to the Rietveld analysis. The temperature dependence of the lattice parameters $a_{\text{cub}}$, $c_{\text{tet}}$ and $a_{\text{tet}} \sqrt{2}$ as well as the unit cell volume in a pseudo-cubic setting are plotted versus the temperature in Figure 5. Both parameters $a$ and $c$ increase nearly linearly with $a_{\text{cub}} \approx 1.57 \cdot 10^{-4} \pm 4 \cdot 10^{-6}$ Å/K and $c_{\text{tet}} = 1.35 \cdot 10^{-2} \pm 4 \cdot 10^{-6}$ Å/K up to 600 K. Above 650 K, $a$ increases and $c$ decreases until they match at 768 K, where $a \approx 6.101$ Å. The volume increases linearly with the temperature expansion coefficient of $\alpha_V = 0.00832 \pm 1 \cdot 10^{-6}$ Å$^3$/K.

The structural relationship between tetragonal LiMnAs and the high-temperature cubic form is shown in Figure 6 with the tetragonal structure given in the pseudo-cubic setting. The crystal structure at room temperature form can be described as an alternate stacking of slabs composed of edge connected slightly distorted MnAs$_4$ and LiAs$_4$ tetrahedra. The MnAs$_4$ tetrahedra are slightly smaller than the LiAs$_4$ tetrahedra. At higher temperatures the $c/a$ ratio in pseudo-cubic setting approaches one. At 768 K, all tetrahedra become regular and half of the Li and Mn atoms of each layer exchange positions with each other in such a way that a Half-Heusler structure is obtained. The diffusion of the Li atoms to the Mn sites and vice versa likely occurs via the empty Li$_4$As$_4$ cubes, showing that Li is rather mobile in LiMnAs. There is no perceptible discontinuity in the volume curve at the temperature of the phase transition, and $c/a$ transits smoothly to one. Although

Figure 3. (a) The DSC peak at 771 K with an onset temperature of $T_o = 768$ K corresponds to the phase transformation to the cubic high-temperature phase. (b) Optical bright field image at room temperature showing the domain structure of LiMnAs induced by the phase transformation.

Figure 4. (color online) Observed x-ray powder patterns in the range $14^\circ \leq 2\theta \leq 25^\circ$ of LiMnAs for various temperatures from 373 K to 873 K. The patterns up to 723 K can be indexed primitive tetragonal. At 823 K and above, LiMnAs crystallizes in a face-centered cubic structure.
FIG. 5. (color online) (a) The unit cell volume of LiMnAs ($Z = 4$) increases linearly from 373 K to 873 K. There is no perceptible volume jump at the phase transition temperature. (b) Lattice parameter (from the XRD measurements on LiMnAs) versus temperature for the tetragonal and cubic phases. Below 600 K, the curves are fitted by a linear function. The dashed line at a higher temperature serves as a guide to the eye.

FIG. 6. (color online) Crystal structures of LiMnAs: (a) tetragonal primitive and (b) face-centered.

this fulfills the requirements for a second-order phase transition, the fast exchange of Li and Mn cannot be described by a continuous process. This can therefore be only a first-order phase transition. The measured change in the entropy and the enthalpy at the phase transition temperature is $\Delta H_{\text{trans}} = 2.19$ J/(Kmol) ($\approx 23$ meV/f.u.) and $\Delta S_{\text{trans}} = 2.85$ J/(Kmol). For the magnetic characterization of LiMnAs, neutron powder diffraction patterns were recorded on the E6 Focusing Powder Diffractometer at Helmholtz-Zentrum Berlin, Germany, using the wavelength $\lambda = 2.448$ Å. The measurements were performed at seven different temperatures in the range from 1.6 K to 873 K. Five diffraction patterns in the range of 1.6 K to 300 K correspond to tetragonal and antiferromagnetically ordered LiMnAs. To protect the sample against moisture and oxidation, a 10 mm fused silica tube was filled and sealed under vacuum. A representative neutron powder diffraction pattern obtained at 1.6 K is shown in Figure 7 along with the fit from the Rietveld refinement using the nuclear and magnetic structures. Table III lists crystallographic data obtained from the Rietveld refinements of the crystal structures based on neutron powder patterns at various temperatures. The powder patterns below the ordering temperature reveal Bragg peaks of magnetic order that can be indexed with the modulation vector $\vec{k} = (0, 0, 1/2)$. This corresponds to an antiferromagnetically ordered structure doubling the $c$-axis of the nuclear structure. The refinement in the magnetic space group $P\overline{4}2_12_1/nmc$ (Belov notation) reveals that the magnetic moments at the Mn sites with $3.7 \mu_B$ at 1.6 K are aligned parallel to the $c$ axis. These observations are in good agreement with the previously reported data, except that the magnetic space group was wrongly assigned in Ref. [12]. The low temperature magnetic moment of $3.7 \mu_B$ is smaller than the value of $5 \mu_B$ expected for the high-spin ($S = 5/2$) state of Mn$^{2+}$, assuming a $g$-factor of 2 ($\mu = g \cdot S \cdot \mu_B$).

Figure 8 shows the temperature dependence of the magnetic moment $m$ obtained from the refinement of the neutron diffraction data. All data below 380 K were fitted by the power law of $m(T) = m_0 (1 - T/T_N)^{\beta}$ with Néel temperature, $T_N = 373.77$ K and the critical exponent $\beta = 0.239$. Regarding the magnetism of LaOMnAs, in Ref. [13] it was found that it is antiferromagnetically ordered in the $ab$ plane, similar to LiMnAs, according to neutron diffraction analysis at lower temperatures. The small increase in the magnetic moments was explained [14].

FIG. 7. (color online) Observed neutron powder pattern (points) for LiMnAs at 1.6 K with the fit of the Rietveld refinement of the nuclear and magnetic structure. The markers of the Bragg reflections for the nuclear reflections (short lines), magnetic reflections (long lines), along with the difference curve are shown at the bottom. The inset shows the alignment of the magnetic moments along the $c$ axis.
TABLE III. Crystallographic data for tetragonal antiferromagnetically ordered and tetragonal paramagnetic LiMnAs and for the high temperature cubic phase of LiMnAs. The z parameter for As in the antiferromagnetically ordered structure is half of that of the paramagnetic structure. In a cubic setup it is defined as $1 - z = \frac{1}{4}$. For comparison, the magnetic moment of Mn$^{2+}$ determined from neutron diffraction measurements is also given together with data from Ref. 12. The residual factors, $R_b$, for the magnetic and nuclear parts are not provided because they are nearly equal for each measurement (approximately 6%).

| $T$[K] | $a$ [Å] | $c$ [Å] | $V$[Å$^3$] | $z$ | $m$[$\mu_B$] |
|-------|---------|---------|------------|-----|--------------|
| 1.6   | 4.262(1) | 12.338(1) | 224.12   | 0.3787(5) | 3.72(3) |
| 10    | 4.262(1) | 12.338(1) | 224.12   | 0.3795(5) | 3.68(3) |
| 13$^{12}$ | 4.253(1) | 12.310(1) | 222.66   | 0.3800(1) | 3.75(3) |
| 30    | 4.262(1) | 12.338(1) | 224.12   | 0.3796(5) | 3.70(3) |
| 50    | 4.261(5) | 12.337(9) | 224.00   | 0.3789(1) | 3.61(3) |
| 293$^{12}$ | 4.267(1) | 12.356(1) | 224.97   | 0.3800(1) | 2.59(2) |
| 300   | 4.259(2) | 12.333(4) | 223.70   | 0.3813(1) | 2.63(3) |
| 317   | 4.269(2) | 12.363(4) | 225.20   | 0.3792(1) | 2.40(3) |
| 322   | 4.269(2) | 12.366(4) | 225.40   | 0.3796(1) | 2.41(3) |
| 332   | 4.270(2) | 12.372(4) | 225.60   | 0.3778(1) | 2.25(3) |
| 348   | 4.272(2) | 12.374(4) | 225.80   | 0.3771(1) | 2.05(3) |
| 352   | 4.273(2) | 12.374(4) | 225.80   | 0.3800(1) | 1.90(3) |
| 357   | 4.274(2) | 12.377(4) | 226.00   | 0.3783(1) | 1.74(3) |
| 362   | 4.273(2) | 12.380(4) | 226.00   | 0.3799(1) | 1.61(3) |
| 366   | 4.276(2) | 12.380(3) | 226.40   | 0.3802(4) | 1.49(3) |
| 370   | 4.275(3) | 12.383(3) | 226.20   | 0.3783(4) | 1.15(3) |
| 373   | 4.275(2) | 12.382(3) | 226.20   | 0.3814(3) | 0.91(3) |
| 393$^{12}$ | 4.273(1) | 12.370(1) | 225.86   | 0.3800(1) | 1.59(3) |
| 423$^{12}$ | 4.279(1) | 12.370(1) | 225.86   | 0.3800(1) | 1.59(3) |
| 573   | 4.289(5) | 6.203(0)  | 114.11   | 0.7582(1) | - |
| 873   | 6.155(4) | -        | 233.18   | $\frac{1}{4}$ | - |

* magnetic moment not compatible with our data.
crystal monochromator. The near edge region of 6510-6560 eV was measured with a minimal step size of 0.25 eV, and the EXAFS regime was measured up to 7540 eV. A mass of approximately 10 mg of powdered Mn compounds with a particle size of $\leq 20 \mu m$ were diluted with $B_4C$ powder and mixed with polyethylene powder. The mixture was pressed to form a pellet with a diameter of 10 mm. All of the handling was performed under an argon atmosphere in a glove-box. Reference data were measured simultaneously with a Mn-foil. This spectrum serves as an external reference for energy calibration and Mn valency. Figure 9 shows the EXAFS signal, $\chi(k)$, and the corresponding Fourier transform. The EXAFS data were analyzed in accordance with the standard procedure for data reduction, using IFEFFIT. The FEFF program was used to obtain the phase shift and amplitudes. The EXAFS signal $\chi(k)$ was extracted and Fourier-transformed (FT) using a Kaiser-Bessel window with a $\Delta(k)$ range of 7.0 $\AA^{-1}$. The $\chi(k)$ curve shows the characteristic pattern for this compound. The FT pattern shows one broad peak at approximately 2.2 $\AA$ (uncorrected for the phase shift), which corresponds to the Mn–As and Mn–Mn scattering contributions. The Mn–Li scattering contribution is also included in this region; however, it does not have a strong influence on the main peak. The grey line in Figure 9 represents the best fitting curve of the data. The structural parameters obtained from the Rietveld refinement were used as the input data to generate the cluster of atoms used. Only single scattering events were considered in the fitting procedure. The excellent agreement between the data and the theoretical structure was accomplished by the low $R$ factors ($\leq 0.6\%$).

A quantitative analysis extracted from the EXAFS data is summarized in Table IV. The amplitude-reduction term ($S_0$)$^2$ used was 0.75. The Mn–As and Mn–Mn distances are slightly contracted by $\leq 2\%$ and the Mn–Li by $\approx 7\%$ compared to the crystallographic data.

In Table IV, the distances obtained by the neutron-diffraction refinement are compared with the EXAFS data. The oxidation state of Mn in LiMnAs was obtained by using the XANES analysis with a widely used method as described by Wong et al. This method considers the determination of the edge shift in relation to the Mn$^0$ edge energy for a given compound. In this case, there is a linear relation between this energy shift and the oxidation state. Using the oxidation state and energy shift of some standard oxides (Mn$_2$O$_3$ and MnO in this case), it is possible to find a linear relation, and obtain the oxidation state for the compound (Figure 10). This method reveals an oxidation state of Mn in LiMnAs of 1.6. Such a decrease in the oxidation state can be expected from weak homonuclear Mn–Mn interactions in the $ab$ plane. This is supported by DFT calculations (see below), which show a considerable interaction in the planes of Mn atoms, affecting their hybridization.

### Table IV.
Quantitative results for LiMnAs from the EXAFS data analysis for the Mn $K$ edge, considering the coordination numbers ($CN$) of the crystal structure. The best fitting exhibits the next-neighbor distances ($R$), mean square displacement in $R \sigma^2$, and $R$-factor for the whole fit.

| Shell Element | $CN$ | $d$ [Å] | $R_{EXAFS}$ [Å] | $\sigma^2$ [Å$^2$] | $R$ [%] |
|---------------|------|---------|-----------------|-------------------|------|
| 1st As        | 4    | 2.601   | 2.550           | 0.006             |      |
| 2nd Mn        | 4    | 3.012   | 2.953           | 0.006             | 0.6  |
| 3rd Li        | 2    | 3.085   | 2.870           | 0.006             |      |

C. DC-resistivity

The resistivity of polycrystalline LiMnAs was recorded using the "Van der Pauw" method in the temperature range of 50-300 K. For LaOMnAs, the electrical resistivities $\rho(T)$ from 100-400 K were obtained by a standard linear four-point contact method. The measurement was performed by means of a physical property measurements system (PPMS, Quantum design model 6000, supported by LOT Germany). Bars of LaOMnAs $2 \times 2 \times 8$ mm$^3$ were cut from pellets obtained by a spark plasma sintering.
with a small activation energy of approximately half of 0.20 eV for LiMnAs and an E_g of 0.57 eV for LiMnAs and an E_g of 1.07 eV for LaOMnAs respectively, at higher temperatures.

Figure 12 shows the resistivity as a function of temperature on a logarithmic scale. We note in particular, that the electrical resistivity changes by more than five orders of magnitude for LiMnAs in the temperature range of 100–250 K and by about two orders of magnitude for LaOMnAs from 150–350 K.

D. Dielectric permittivity

Ellipsometric measurements covering the far-infrared to deep-ultraviolet spectral range (10 meV–6.5 eV) were carried out at room temperature on LaOMnAs ceramic dense pellets polished to an optical grade finish. The measurements in the near-infrared to deep ultraviolet spectral range (0.75 eV - 6.5 eV) were performed with a rotating analyzer-type Woollam VASE variable-angle ellipsometer. For the infrared measurements from 0.01 eV to 1.0 eV, we used home-built ellipsometers in combination with a Bruker Vertex 80v FT-IR spectrometer. Some of the experiments were performed at the infrared IR-1 beamline of the ANKA synchrotron light source at the Karlsruhe Institute of Technology, Germany. The complex dielectric function, \( \tilde{\varepsilon}(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \) was directly determined from ellipsometric angles \( \Psi(\omega) \) and \( \Delta(\omega) \). The inversion of the ellipsometric data was performed within the framework of an effective medium approximation, which in the case of polycrystalline samples corresponds to the volume average of the anisotropic dielectric tensor projections. We did not take into account the surface roughness grain texturing effects on \( \tilde{\varepsilon}(\omega) \), which is estimated to be less than 10% over the measured spectral range. Because of the air sensitivity, it was not possible to obtain ceramics of LiMnAs sufficiently dense for optical measurements.

Figure 13 shows the complex dielectric function of the
LaOMnAs sample at $T = 294$ K. In the far-infrared range, there are six strong phonon modes. The lowest interband transition in this material lies above 0.4 eV. One can clearly distinguish three optical bands peaked at $\sim 1.4$, $\sim 2.1$, and $\sim 3.2$ eV. These transitions provide the main contribution to the static permittivity and form the direct absorption edge, below which the real part of the dielectric permittivity becomes nearly constant down to the phonon frequencies, $\varepsilon_1(0.2$ eV $\lesssim \omega \lesssim 1.2$ eV) $\approx 8$. We note that the main features resemble those that characterize the interband electronic contribution to the dielectric function of polycrystalline LaOFeAs, while shifted by $\sim 0.7$ eV to higher energy. The rise of $\varepsilon_2(\omega)$ above 0.4 eV can be attributed to indirect interband transitions.

FIG. 13. (Left) Phonon and (right) interband electronic contribution to the real and imaginary parts of the dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ of LaOMnAs measured at $T = 294$ K. Arrows mark the peak positions of the main absorption bands.

E. DFT calculations

In order to gain further insights into the electronic structure and energetics of LiMnAs and LaOMnAs, we have performed ab-initio calculations based on the density functional theory (DFT) with the VASP code. For the approximate treatment of the electron exchange and correlation, we have used the Perdew, Burke, Ernzerhof (PBE) functional together with the projector-augmented wave (PAW) method with a plane-wave cutoff energy of 400 eV. In the irreducible part of the Brillouin zone, the k-point integration was performed on an $8 \times 8 \times 4$ Monkhorst-Pack mesh. To describe the magnetic ordering in the compounds as found from neutron diffraction for the tetragonal antiferromagnetic structures, spin polarized calculations have been carried out for supercells containing four primitive unit cells (see Fig. 1).

In the case of LiMnAs, the calculated local Mn moments of $3.82$ $\mu_B$ for the ground state are in excellent agreement with the value of $3.72$ $\mu_B$ measured at 1.6 K, which is the most representative temperature for a comparison between experiment and theory. As already mentioned in the introduction, the magnetic moment of the Mn atoms is well localized in this class of materials. Based on a fully ionic picture of LiMnAs, i.e. Li$^+$, Mn$^{2+}$, As$^{3-}$, one would expect that the oxidation state of Mn to be $2^+$. The experimentally obtained value of 1.6$^+$ from XANES measurements are somewhat lower than this $2^+$ expected value. Therefore, we have looked into the real-space density of LiMnAs, and apart from the expected $sp^3$ hybridization between Mn and As (see left panel in Fig. 14), we found that there is also a feature present that corresponds to a mixture between Mn–As and Mn–Mn bonding (see right panel in Fig. 14).

From subsequent DFT calculations, we have determined the magnetic exchange coupling constants $J_{ij}$ of the classical Heisenberg model, $H = -\sum_{i>j} J_{ij} \hat{e}_i \hat{e}_j$, where $\hat{e}_i, \hat{e}_j$ are the unit vectors corresponding to the directions of the local magnetization at sites $i$ and $j$. For this purpose, we have employed the SPR-KKR program package which is a suitable numerical tool for such computational task, not relying on pseudopotentials, where $J_{ij}$ can be evaluated within the Green’s function formalism.

As it follows from analysis of the exchange coupling scheme (see Fig. 15), within each Mn plane, the magnetic moments of the nearest neighbors are coupled antiparallel (with $J_1$ $\approx$ $-60$ meV, shown in red), and this strong antiparallel coupling cannot be perturbed by the competing but smaller next-nearest neighbor antiparallel interaction ($J_2$ $\approx$ $-14.7$ meV, shown in dark-red). Thus, within each plane the nearest Mn magnetic moments are ordered antiferromagnetically. Further, to understand how the nearest planes are magnetically oriented to one another, we consider the inter-plane exchange coupling. Both leading constants of the inter-plane exchange are positive, $J_{1,2}$ $\approx$ 0.6 and 0.24 meV, which correspond to the nearest and next-nearest inter-plane interactions, respectively. It is easy to see that for an already fixed in-plane magnetic
FIG. 15. (color online) The scheme of the leading magnetic exchange interactions within the Mn atomic planes and between the nearest Mn atomic planes of LiMnAs. For clarity, only Mn atoms are shown (blue spheres) and the orientations of the magnetic moments are depicted with arrows. The thickness of the bonds connecting interacting atoms are roughly proportional to the strength of the corresponding exchange interactions, where antiferromagnetic and ferromagnetic coupling is represented by red ($J_1, 2$) and green ($j_1, 2$) colors, respectively.

order, these two interactions are also competing. Despite the fact that $j_1 > j_2$, each Mn atom (for simplicity we consider one in the center of Fig. 15) has only 2, but 8 next-nearest inter-plane neighbors, which leads to an overall domination of the next-nearest inter-plane coupling ($8j_2 > 2j_1$); thus, the next-nearest Mn planes are coupled antiferromagnetically.

Based on the Mulliken analysis, the corresponding partial charges, i.e., oxidation numbers of Li, Mn, and As were computed as +0.8, +1.5, and −2.3, respectively. This is again in good agreement with the XANES measurement presented above, where an oxidation state of 1.6 was determined for the Mn atom in LiMnAs. For LiMnAs, in our calculations we found an indirect band gap of 0.55 eV (see Fig. 16 (a)), which is very close to the 0.57 eV gap estimated from the higher temperature range of the Arrhenius plot of the conductivity measurements given in the previous sections. These results are also in a good agreement with the recent full potential calculations for bulk LiMnAs, where within the local density approximation (LDA) a $\Gamma$-M indirect gap of approximately 0.5 eV was computed.

As already shown, at 768 K LiMnAs undergoes a phase transition to the cubic crystal system. Due to computational limitations and difficulties from the perspective of the methodology, the implicit treatment of temperature effects in ab-initio calculations is not straightforward. Therefore, for the study of the cubic phase we have assumed, that the Mn atoms are ordered antiferromagnetically as in the tetragonal phase. Using this model, our calculations indicate, that in contrast to the tetragonal phase, the cubic structure has a direct band gap of 0.84 eV. By comparing the computed total energies of the tetragonal and cubic phases, we found that the cubic phase is only 24 meV higher in energy per formula unit than the tetragonal phase. Thus, although the tetragonal structure is the ground state, the tetragonal-to-cubic phase transition can easily take place. This is because the two phases are rather close in energy, and the energy difference of 24 meV is lower than the 75 meV thermal energy of the system at 768 K, which means that the system can easily surmount the energy difference of 24 meV. Hence, there is good agreement between the theoretically estimated energy difference and the experimentally measured 23 meV/f.u. change in enthalpy, which justifies the use of the simplified theoretical model. Our calculations suggest that AFM...
ordering dominates in LiMnAs so strongly, to the extent that even if LiMnAs could be synthesized in the cubic phase, the pure undoped compound would still be an AFM semiconductor.

In the case of LaOMnAs, the theoretical local moments as obtained with the PBE functional for the Mn atoms are 3.54 $\mu_B$. In contrast to these results, via neutron diffraction measurements performed at 290 K, the refined magnetic moment of Mn was 2.43 $\mu_B$, which is more than one $\mu_B$ lower compared to our theoretical result. In a later experiment, however, it was shown that the moments at 2 K are 3.34 $\mu_B$, which is in good agreement with our calculations. In the case of LiMnAs, our neutron-diffraction data also show a similar trend as a function of temperature, where at 300 K the Mn moments are reduced from 3.72 to 2.62 $\mu_B$ (see Table 1). Furthermore, in case of the structurally closely related BaMn$_2$As$_2$ the Mn local moments were determined to be 3.88 $\mu_B$ at 10 K. Hence, the magnetic properties and magnetic moments are rather similar in the whole family of the AMnAs ($A = Li, LaO, Ba,$ etc.) layered structure type.

The computed oxidation state of the La, O, Mn, and As atoms are $+2.4, -0.8, +1.4,$ and $-3.1$, respectively, i.e., the oxidation state of O is underestimated, and that of As is overestimated. Regarding the electronic structure, we found that LaOMnAs is also an indirect band-gap semiconductor with an $E_g$ of 0.46 eV (see Fig. 16 (b)), which is considerably lower than the value of 1.07 eV derived from the Arrhenius plot.

### III. CONCLUSION

In summary, in this paper, we have presented a broad overview of the synthesis, atomic and electronic structure, and magnetic properties of LiMnAs, LaOMnAs, and other related compounds in the AMnX family. Thus, with this work, we respond to several important questions raised concerning this important class of materials. In general, the compounds in the AMnX family can be classified in two main categories: AFM semiconductors and FM metals. The nature of the magnetic coupling and of the semiconducting or metallic behavior is mainly determined by the shortest Mn–Mn distances ($d_{Mn-Mn}$), which seems to be a general property of the compounds containing MnAs layered networks.

For LiMnAs and LaOMnAs, our data are in good agreement with the literature, showing that both are antiferromagnetic semiconductors, with a magnetic moment of ca. 4 $\mu_B$ per Mn atom at low temperatures. Interestingly, by combining thermal analysis and temperature dependent XRD measurements, a phase transition to the cubic Half-Heusler phase has been discovered. Theoretical calculations suggest that even if cubic LiMnAs could be stabilized, the ideal undoped cubic counterpart would still be an AFM semiconductor, similar to the tetragonal compound. EXAFS and XANES measurements indicate the oxidation state of Mn to be 1.6. This is in agreement with the concept of localized moments on Mn and explains the close relationship between the cubic and tetragonal phase and the connection between Mn and rare earth ions in tetragonally coordinated structures. Regarding the weak ferromagnetism, in contrast to Refs. 13 and 21, due to symmetry considerations, we expect that canting takes place at the surfaces and interfaces of LiMnAs and LaOMnAs, but in the bulk this is unlikely.

Resistivity measurements on LiMnAs and LaOMnAs show two distinct regions of activated transport behavior, and a large change in resistivity by more than five and two orders of magnitude, respectively. Furthermore, we have shown that LaOMnAs is also a promising material for the realization of spin valves, and our findings suggest that compounds such as BaMn$_2$As$_2$ and related compounds are promising candidates as well.

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