Preparation of a Novel Polymer Blend of Poly(ethylene oxide) and the Inorganic Polymer $(Mo_3Se_3^-)_\infty$: Infrared Absorption of Thin Films

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Polymer blends of $LiMo_3Se_3$ and poly(ethylene oxide) (PEO) were formed. Thin films of the above blends containing individual infinite $(Mo_3Se_3^-)_\infty$ chains were deposited on polyethylene substrate, and their transmittance in the far infrared was measured. We discuss the implications of the infrared response to the conducting properties of the chains. The question of the electron localization in this one-dimensional system is examined.

Introduction

The quasi-one-dimensional compounds MMo_3Se_3, M = Li, Cs, Tl, K, and Rb, are members of a broader family of cluster compounds[1] with remarkable properties.[2] Of special interest to us in this paper is the compound $LiMo_3Se_3$. Their structure, given in Figure 1, consists of infinite $(Mo_3Se_3^-)_\infty$ chains running along the *c* axis, separated by columns of M^+ ions.[3] The size of the ion M^+ determines the distance between the chains. Depending upon the strength of the interchain interaction, the chains behave as either one- or three-dimensional conductors.[2] Strongly interacting chains will give rise to highly anisotropic three-dimensional compounds. This is the case with $TlMo_3Se_3$ which is metallic and becomes superconducting[2] at 5.6 K. For weakly interacting chains the compounds have a one-dimensional nature. Band structure calculations of the infinite chains[4,5] in the one-dimensional compounds show that the Fermi level is in the middle of a half-filled band. Such 1-D compounds, at low temperatures, may undergo a "Peierls distortion", leading to a semiconducting ground state. Indeed, some of the compounds where M^+ is electropositive (M = Rb, Cs) show a metal–semiconductor type "transition" around 100 K.[2]

The highly anisotropic properties of the above compounds reflect the properties of the individual chains as modified by their mutual interactions. Therefore, it is of interest to examine the existence and properties of individual, isolated chains. The one-dimensional $LiMo_3Se_3$ compound dissolves in highly polar solvents,[6] leaving the chains intact in solution. This demonstrates the individuality of the chains and their ability to form purely inorganic polymer solutions.

The chains are composed of staggered stacks of Mo_3Se_3 triangular units (FIgure 1). The Mo atoms form face sharing octahedral along the *c* axis while the Se atoms cap the remaining faces. The Mo–Mo distance in the chains is 2.78 Å, which is slightly less than the Mo–Mo distance in the Mo metal. Such a distance indicates strong metal bonding between the Mo atoms within the chains. Electrons delocalized along the chains result in their conducting properties.[4,5]

In this paper we study the infrared properties and the electrical resistance of the weakly interacting individual chains by exploiting their ability to form polymer blends with organic polymers. The resistance was derived from the measured infrared transmittance of thin films of polymer blends. The possibility of electron localization in this one-dimensional system is analyzed.

Experimental Section

Preparation of $LiMo_3Se_3$. Polycrystalline $LiMo_3Se_3$ was prepared by two methods from polycrystalline $In_2Mo_6Se_6$ that had been previously synthesized from the elements. The methods were chosen with the objective of enhancing the crystallinity and the size of the crystallites. The larger the crystallites, the longer the length of the chains will be. Method one proceeded by ion exchange in a LiI melt according to the reaction[7]

$$In_2Mo_6Se_6 + LiI \xrightarrow{600\ °C} LiMo_3Se_3 + InI \qquad (1)$$

One end of the reaction tube was maintained at <300 °C to collect the InI sublimed off and to drive the exchange process. In general, the reaction was quite slow, requiring approximately 3 weeks and two or three regrindings to get complete ion exchange. Excess Li was removed from the $LiMo_3Se_3$ by several thorough washings in acetonitrile.

The second method involved a two-step process, cation removal followed by Li intercalation. Mo_3Se_3 was prepared by the treatment of $InMo_3Se_3$ with flowing HCl gas at 400 °C as follows:

$$InMo_3Se_3 + HCl \xrightarrow{400\ °C} Mo_3Se_3 + InCl + \tfrac{1}{2}H_2 \qquad (2)$$

The reaction proceeds rapidy (about 6 h). The InCl formed in the process evaporates from the hot zone and condenses on the reaction tube walls near the ends of the furnace. Complete removal of the indium was verified by the weight difference between the Mo_3Se_3 formed and the $InMo_3Se_3$ starting material. Formation of $LiMo_3Se_3$ was accomplished by treatment of the Mo_3Se_3 formed above with excess butyllithium (BuLi) in hexane according to the reaction

$$Mo_3Se_3 + BuLi \rightarrow LiMo_3Se_3 + C_8H_{18} \qquad (3)$$

The excess BuLi solution was decanted and the polycrystalline

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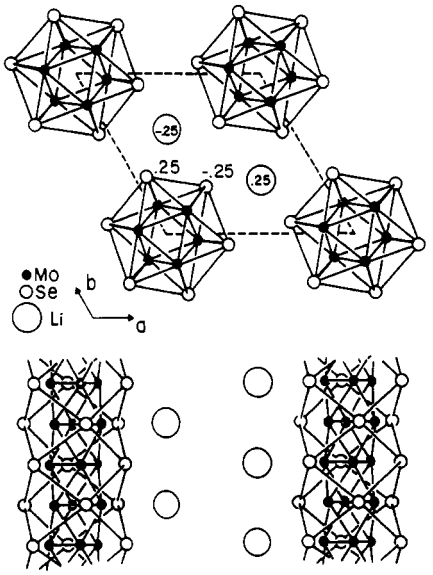

Figure 1. Structure of $LiMo_3Se_3$ and the side view of the infinite $\{Mo_3Se_3^-\}_\infty$ chains separated by columns of Li^+. The chains are composed of staggered stacks of Mo_3Se_3 units.

$LiMo_3Se_3$ was washed three or four times with dry acetonitrile, vacuum dried, and stored in a tightly sealed vial in the glovebox. The size of the needlelike crystallites was estimated to be on the order of 10–100 μm in length, although occasionally visibly large crystals were formed. $LiMo_3Se_3$ prepared by either method was completely dissolved in polar solvents with dielectric constant $\epsilon > 45$, giving dark red, weakly air-sensitive solutions according to the reaction

$$n\mathrm{LiMo_3Se_3} + \text{polar solvent} \rightarrow n\mathrm{Li^+} + \{\mathrm{Mo_3Se_3^-}\}_n \quad (4)$$

In ref 6, transmition electron micrographs on films dried out from dilute solutions reveal that the remaining material is composed of fibers of length ≈ 10 μm, i.e., equal to the size of the starting crystallites. This also reflects the length of the chains in the solution. Since our solution satisfy the same conditions as ref 6, we contend that the chains are left intact in solution, constituting a purely inorganic polymer solution.[6] Their length ranges as high as 10–100 μm, corresponding to $n > 40\,000$. In dilute solutions, the chains are not expected to make physical contact with each other because their average separation is large and because they repel each other due to their negative charge.[6] Therefore, the chains behave like free-floating, 6-Å-diameter, charged wires (polyanions). We will examine later if these wires are metallic.

It appears that the solvation of the chains is achieved because of the large solvation energy of Li^+ ions.[6] The chains follow into the solution in order to achieve electroneutrality, resulting in this unusual "inorganic polymer solution". Polar solvents that result in dissolution include dimethyl sulfoxide (DMSO), *N*-methylformamide (NMF), propylene carbonate (PC), and water. The resulting solutions are stable for a year or more as long as oxygen is excluded from the initial solvent and solution. DMSO was mostly used in the preparation of polymer blends. We purified DMSO by stirring over BaO overnight and refluxing and distilling from the BaO under reduced pressure.[8]

Polymer Blends. By choice of the appropriate solvent, uniform solutions containing both organic polymers and the $\{Mo_3Se_3^-\}_\infty$ chains can also be formed. Polymer blends were prepared by mixing solutions of $LiMo_3Se_3$ in purified[8] DMSO with that of organic polymers containing polar groups, such as poly(ethylene oxide) (PEO) or poly(vinylpyrrolidone) (PVP). Homogeneous solutions were formed after several hours of stirring. The resulting solutions produced optically homogeneous films (to 500×). Solutions resulting from the addition of a nonpolar organic polymer such as polystyrene tended to remain nonhomogeneous as evidenced by the presence of small, clear, circular regions of polymer in dried films of the solution. The viscosity of the polymer blend solution was highly dependent on the organic polymer used. Slight increases in the viscosity were observed for PEO, while solutions with a 4:1 poly(vinylpyrrolidone) to $LiMo_3Se_3$ ratio gelled after about 30 min of stirring.

Evaporating the solvent, we made thin films of a polymer blend of the organic polymer and the inorganic polymer, containing infinite chains, with very interesting intermediate properties. The organic polymer acquires some of the properties of the chains such as electrical conductivity or optical absorption in the far infrared. We will use these properties in order to study the properties of the individual chains.

Film Preparation. Samples prepared for far-IR studies were made from solutions of $LiMo_3Se_3$ in DMSO (7.5×10^{-3} M) and PEO (average molecular weight of 100 000) in acetonitrile (7.5×10^{-2} M) mixed in a 1:6 ratio per weight, respectively. The roughly estimated monomer ratio is on the order of 1:10. After this stirred for several days, films were cast from the homogeneous solution on a 0.05-mm-thick polyethylene sheet and placed in a vacuum desiccator, which was slowly evacuated to prevent splattering of the solution during solvent removal. Samples were dried at room temperature under dyamic vacuum (liquid N_2 trap) for approximately 48 h. The thickness of the resulting films was 0.1 mm. Differential scanning calorimetry (Figure 2) revealed that sampls prepared in this manner contain small amounts of tightly bound DMSO, presumably still coordinated to Li, and about 10–15% uncoordinated PEO. In the first DSC run an endothermic peak appears, around 70 °C, reflecting the sublimation of DMSO and drastically diminishes with heating cycles. However not all the DMSO can be extracted from the films by heating. Even heating of the polymer blends to 150 °C under dynamic vacuum for 4 h failed to completely remove the bound DMSO. The broad exothermic-like peak in the first DSC run is a consequence of the extraction of DMSO because it does not appear in the subsequent heating cycles. We speculate that it is a result of the rearrangement of the polymer chains. X-ray diffraction patterns show several broad reflections, none of which corresponds to those of either PEO or $LiMo_3Se_3$. The pattern is a characteristic pattern of an amorphous film. Inspection of the films with an optical microscope did not reveal inhomogeneities on the scale of 1 μm.

Because of the small concentration of the starting inorganic material in the organic polymer blend solutions, the chains are well separated in space. The organic polymer also prevents the chains from clustering together as happens in high concentration inorganic polymer chain solutions.[6] From the wave vector corresponding to the maximum of the structure factor, we can estimate the average distance between the chains in the films to be more than 13 Å, almost double their distance in a crystal. The large separation significantly reduces the chain–chain interaction in comparison to that found in MMo_3Se_3 solids. The organic polymer macromolecules constitute helicoidal chains that intervene between the Mo_3Se_3 chains, further screening the chain–chain interaction. The Li^+ ions are thought to be coordinated to the polar groups of the organic polymer, as in solutions of PEO with Li salts,[9] giving the polymer macromolecules positive charge. However, their charge is partially screened, and the interaction between the chains and the organic host is expected to be weak although largely ionic. Therefore, the electronic coupling between the inorganic chains in the blend and between the chains and the organic host is weak, and the material, should display one-dimensional character.

Optical Measurements. The transmittance of the films (FIgure 3) was measured at room temperature by using an IBM IR 98 modulation interferometer (Bruker interferometer). The transmittance was measured relative to a "blank" consisting of the PE substrate and a film of pure PEO of the same thickness as that of the blends. Corrections due to multiple scattering from the front and back surface of the film were properly taken into account. The multiple reflections were treated incoherently. Using Drude's model to describe the polarization of the chains, we find the plasma frequency and the relaxation time of the

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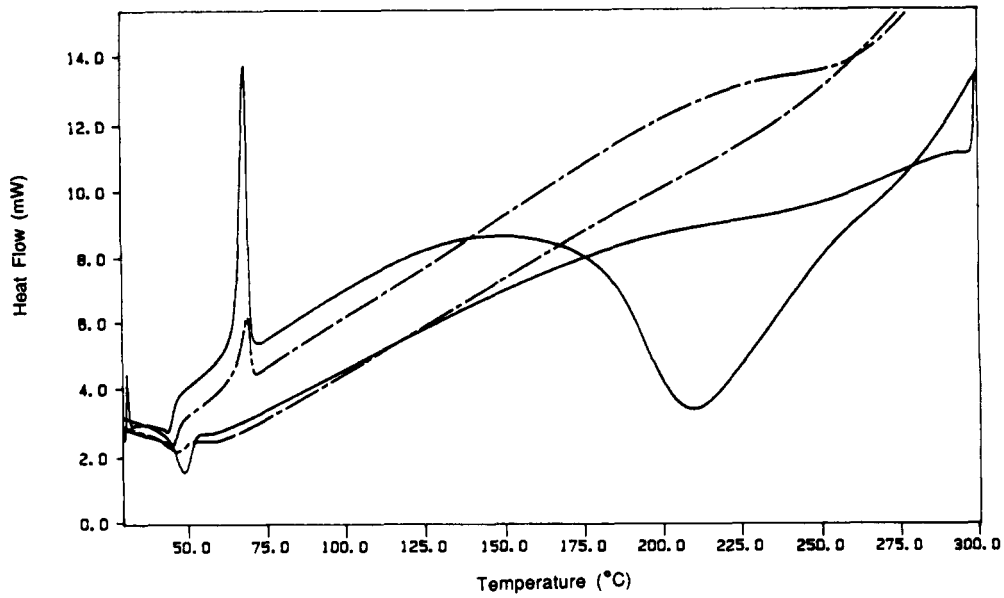

Figure 2. Differential scanning calorimetry pattern of polymer blends of poly(ethylene oxide) and $LiMo_3Se_3$. The solid line is the first run. The dashed line is the second run on the same film. The heating rate was 10 °C/min for both films.

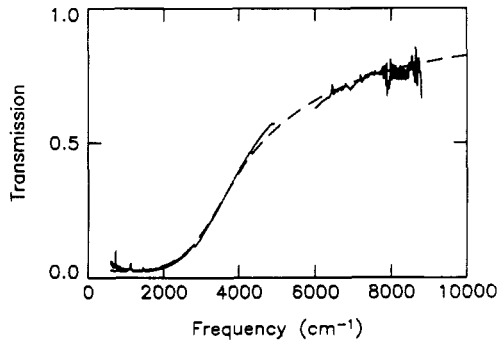

Figure 3. Transmittance of thin films of polymer blends of poly(ethylene oxide) and $LiMo_3Se_3$. The dashed line is a fitting according Drude's model with parameters $\omega_p = 4300$ cm^{-1} and $\tau^{-1} = 1500$ cm^{-1}.

carriers by fitting the model to the measured transmittance curve.

Results and Discussion

As Figure 3 shows, the transmittance is very low (<5%) near 2000 cm^{-1} and slowly rises to about 80% at 8000 cm^{-1} and above. The only phonon modes in this region of the spectrum are the C–H stretching modes in PE and PEO. These are typically near 3000 cm^{-1}. They appear as a very sharp narrow peak in the spectrum of the bare substrate. Such modes due to the PE and PEO should not be observed in these measurements since the "blank" has the same thickness as the sample and the measurements are taken relative to the "blank". All other phonon modes have frequencies less than 2000 cm^{-1} because of the bigger masses of the atoms involved. Thus, it is apparent that the broad decrease in transmittance as the frequency is lowered bellow 8000 cm^{-1} is due to an interaction of the radiation with the electronic states in $(Mo_3Se_3^-)_n$ chains.

Since the transmission is high at higher frequencies, it is unlikely that the spectrum of Figure 2 is due to interband transitions. However, from the published 1-D band structure calculations[4,5] it is apparent that interband transitions are possible in this frequency range, beginning at approximately 1000 cm^{-1} for indirect transitions and 4000 cm^{-1} for direct transitions. The joint density of states that we estimate from the band structure in fact should show a sharp maximum at 6000–7000 cm^{-1} due to a direct transition at the γ point. Since all of these features would lead to decreasing transmission with increasing photon energy, this cannot be the source of the present anomaly. The only plausible source of the observed spectrum is a plasma edge.

Assuming no interband transitions or interchain interactions, we use Drude's model to find the carrier relaxation time τ and the plasma frequency $\omega_p^2 = 4\pi e^2 n/m^*$, where n is the electron density and m^* is the effective electron mass. The fitting is sensitive to the value τ but is less sensitive to the value of ω_p. Good fits are obtained when ω_p is (1.3–3.3) $\times 10^{14}$ s^{-1}, while $\tau = 2.2 \times 10^{-14}$ s.

In the simplest case, in which each Mo_3Se_3 unit contribute one free electron confined to the chain and the effective electron mass is equal to one electron mass, the calculated charge density is $n = 1.6 \times 10^{22}$ cm^{-3} and the plasma frequency would be $\omega_p = 7 \times 10^{15}$ s^{-1}. If we assume that the electronic charge should be averaged over the whole volume, including the space between the chains occupied by PEO, then $n = 3.3 \times 10^{21}$ cm^{-3} and $\omega_p = 3.3 \times 10^{15}$ s^{-1}. In both cases ω_p is an order of magnitude higher than the value obtained by fitting the data, raising the question what shifts the plasma edge to lower frequencies.

Assuming that the chains in solution are metallic, there are two factors that could lead to an apparent shift in the plasma frequency from the free electron value. Interband transitions at frequencies below ω_p will shift the observed edge to lower frequencies. Furthermore, it may be necessary to treat the chains in PEO in an effective medium theory.[10,11] In general, this could lead to a spectrum of plasma resonances due to interparticle coupling. Also, the chains are quite close together when compared to the radiation wavelength, and at the same time their lengths are comparable to the wavelength. To our knowledge, an effective medium theory has never been solved in this limit.

If, tentatively, we use the measured τ and the free electron ω_p estimated above, the electron mean free path is $l = 200$ and 120 Å, respectively, and the resistance of the chains if $\rho = 10$ and 50 $\mu\Omega$ cm, respectively, suggesting that the chains are highly conducting metals (as good as Cu). In both cases the estimated resistance is much smaller than the resistance of the interacting chains in the solid.[2]

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This conclusion is probably not correct. The resistance of noninteracting chains is expected to be higher than the resistance of the interacting chains. Next we will try to identify the conditions and the parameters that determine the electrical behavior of the chains.

The dc conductivity of the chains is given by the formula

$$\sigma = \omega_p^2 \tau / 4\pi$$

Using the values of ω_p and τ determined from the data on the films, we find the resistivity of the chains to be

$$\rho_{exp} = 10^3\text{–}10^4\ \mu\Omega\ \text{cm}$$

which is 1–2 orders of magnitude higher than the measured resistivity[2] of solid MMo_3Se_3 (M = Rb, Cs, Tl) compounds that reflect the resistivity of the chains imbedded in a crystal lattice. This value is also higher than the resistance corresponding to the minimum metallic conductivity of disordered metals. Therefore the description of the electrical properties of the chains by a free electron gas may be inadequate. In a highly resistive solid the electron motion is rather diffusive, and they are scattered incoherently. However, we can apply the results of the free electron gas if we consider the effective mass of the electrons.

If we consider that each Mo_3Se_3 unit contributes one electron to the half-filled conduction band, as band structure calculations show,[4,5] then we can find the electronic charge density. From the plasma frequency obtained with Drude's model, we find an electronic effective mass to be of the order of 1000, i.e., $m^*/m = 10^3$. The mean free path of the conduction electrons can be found by using the relation $l = hk_F\tau/m^*$, where k_F is the Fermi wave vector and can be calculated from the charge density. The mean free path calculated from the above values is of the order of the interatomic distance, i.e., $l = 2.25$ Å. With the above numbers it is easily demonstrated that the Ioffe–Regel[12] condition $lk_F \sim 1$ is satisfied, suggesting that the system is near the onset of localization.

The above conclusions are sensitive to the value of the plasma frequency. Its value as measured above would be unquestionable if the absorption spectrum was due to only to the conduction electrons. However, interband transitions can affect the absorption spectrum and shift it toward lower frequencies. Indeed, empty bands lie close to the Fermi level[4,5] within the energy range of the absorbed photons. Therefore, it is possible that the plasma frequency is underestimated by as much as a factor of 10 if the interband transitions are not properly taken into account. Assuming this higher value of plasma frequency, we estimate the mean free path to be of the order of 10 unit cells long, and the resistivity of the chains to be of the order of 10^2 $\mu\Omega$ cm (in the range 50–300 $\mu\Omega$ cm). The resistance of the chains thus determined is close to the resistance of 150–450 $\mu\Omega$ cm of the three-dimensional chains imbedded in a solid.[2] For agreement with the experiment, we have to conclude that if the plasma frequency is indeed higher, the relaxation time of the carriers should be rather short. Since our fitting of the absorption curve is not good for small relaxation times, it seems unlikely that ω_p is shifted by as much as assumed above. We might say that the experimentally determined plasma frequency and the relaxation time have accuracy higher than 50%.

An alternative treatment, consistent with the low plasma frequency, the heavy electron mass, and the short electron mean free path is the following: Since the chains are very resistive, the Ioffe–Regel condition is satisifed. From this condition and the definitions of the plasma frequency and the mean free path, assuming that the measured values of ω_p and τ are the correct ones, we can calculate self-consistently the Fermi wave vector and the mean free path. From these values we can calculate the charge density of the carriers to be 2.3×10^{21} cm^{-3}. This value is 1 order of magnitude smaller than the value calculated earlier from the geometry of the chains. This low charge density is understandable now, since the motion of the carriers is incoherent and not all the electrons participate in conduction. From the above density and the volume of the chains we can find the effective number of electrons per unite Mo_3Se_3 to be $\sim$0.2, i.e., only 20% of the electrons participate in the conduction.

Summary

In conclusion, it seems that the system of infinite chains is close to localization. Only a fraction of the carriers contribute to conduction, and the electrons strongly interact with the lattice, hence their heavy mass.

However, the observation of the plasmalike edge in the transmition spectrum of the PEO–(Mo_3Se_3) polymer blend suggests that the chains are still metallic even though they are 6 Å in diameter. While these data are suggestive they are not conclusive. Further studies over a much broader frequency range are needed and are planned. If, however, our suggestion is correct, it would seem that these wires are not insulating even though they would be considered to be in an extreme one-dimensional limit. More experiments at low temperatures will demonstrate if these wires become insulators by undergoing Peierls distortion and thus complete the picture of electron conduction in 1-D chains.

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